





THE  
DEVELOPMENT  
AND  
PRESENT ASPECTS  
OF  
STEREO-CHEMISTRY.

BY  
CHARLOTTE F. ROBERTS, PH.D.

BOSTON, U.S.A.  
D. C. HEATH & CO., PUBLISHERS.  
1896.

FEB 25 1941

200554

COPYRIGHT, 1896,  
BY CHARLOTTE F. ROBERTS

Gift of Chemistry Dept  
to  
Chemistry Library

CHEMISTRY LIBRARY

QD

481

R64

UNIVERSITY PRESS:  
JOHN WILSON AND SON, CAMBRIDGE, U. S. A.



# CONTENTS.

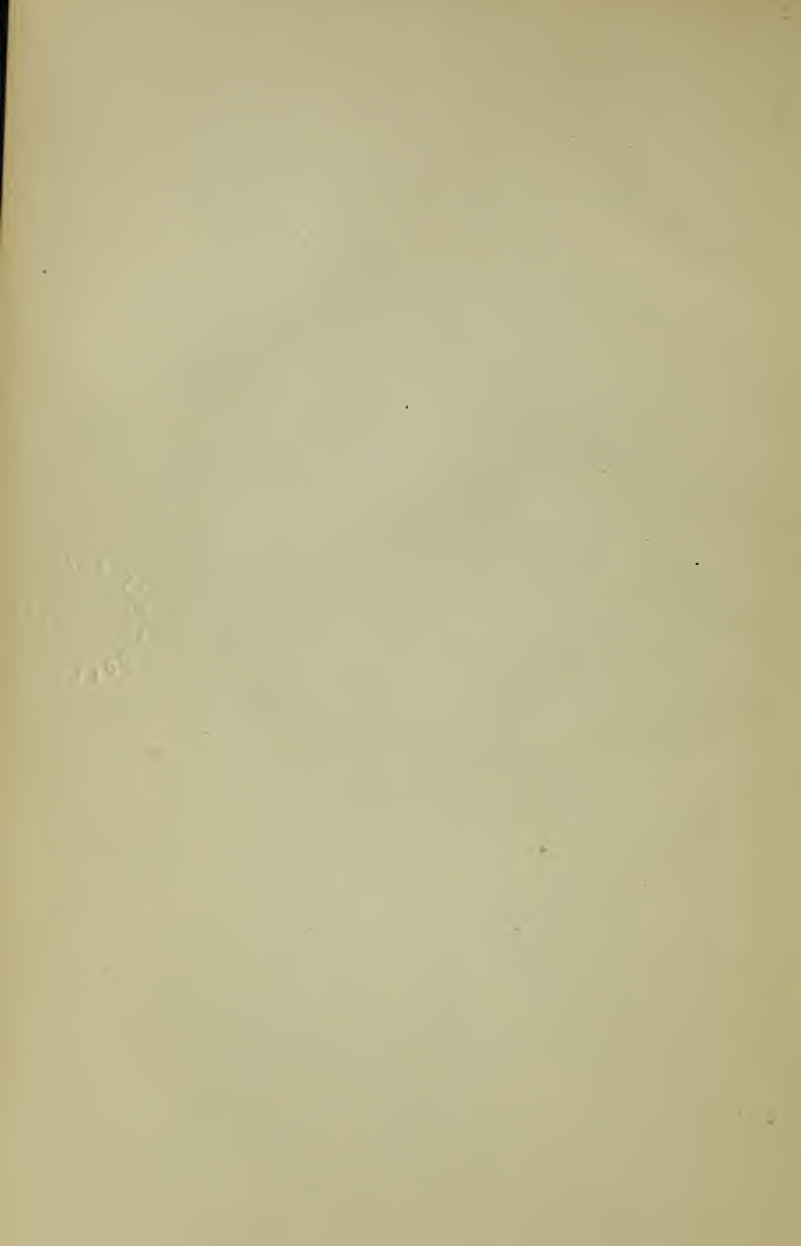
---

	PAGE
I. GENERAL PRINCIPLES OF STEREO-CHEMISTRY . . .	1
II. ILLUSTRATIONS AND APPLICATIONS TO PARTICULAR CASES . . . . .	37
III. THE BENZENE SERIES . . . . .	68
IV. THE STEREO-CHEMISTRY OF NITROGEN . . . . .	105
V. VARIATIONS IN OPTICAL ACTIVITY AND RELATIONS OF STEREO-CHEMISTRY TO CRYSTALLOGRAPHY . .	138
VI. DEDUCTIONS AND SPECULATIONS CONCERNING THE NATURE OF ATOMS AND VALENCE, WHICH HAVE GROWN OUT OF THE STUDY OF STEREO-CHEM- ISTRY . . . . .	153

---

LIST OF BOOKS CONSULTED . . . . . 190

PERIODICALS TO WHICH REFERENCE HAS BEEN MADE 191



# STEREO-CHEMISTRY.



## I.

### GENERAL PRINCIPLES OF STEREO-CHEMISTRY.

SINCE the introduction of the Atomic Theory, great advances have already been made in the definiteness of our conceptions in regard to the internal structure of molecules, and it is largely to the study of the phenomenon of isomerism that this growth is due. There has been a gradual evolution of ideas from the vague conception of matter as continuous, to the idea of matter as made up of definite molecules, separate and distinct, then of these molecules as made up of a definite number of separate and distinct atoms, and finally, through the study of isomerism, to the idea of these atoms as possessing a definite arrangement in the molecule, one atom being directly joined to another, forming a kind of chain. It is this last conception which has given us our ordinary structural formulas; and we must certainly feel that it is a great triumph of human ingenuity when we are enabled to determine the method of atomic linking from a study of the chemical reactions of the body in question.

But the study of isomerism leads us a step further, and gives us a glimpse, at least, of the possible arrangement of the atoms in space, and the geometrical forms which groups of combined atoms assume. This branch of science, known

variously as the study of "Geometrical Isomerism," or "Stereo-Chemistry," or "Chemistry in Space," has been almost entirely developed within the last <sup>forty</sup>~~twenty~~ years, but the literature of the subject scattered through the various scientific journals is already enormous, and the underlying ideas in some form or other are now accepted by most eminent students of Organic Chemistry.

The foundation for much that is now accepted in stereochemical theories was laid by Pasteur in 1860-61. In his "*Recherches sur la dissymétrie moléculaire des produits organiques naturels*," he referred the peculiar optical isomerism of the tartaric acids to a lack of symmetry in the molecule, just as optical activity in crystals is referred to a lack of symmetry in the crystalline individual.

In 1873 Wislicenus gave a new impulse to the discussion of these problems by pointing out the inadequacy of structural formulas to explain the isomerism in the lactic acids. In his investigation of these acids, he found that ordinary and sarco-lactic acids must be represented by the same structural formula, and yet they were undoubtedly two distinct bodies, one being active as regards polarized light, the other inactive. He was thus led to the conclusion that, since the atomic linking must be the same in both, the difference in physical properties could only be accounted for on the supposition of a different relative arrangement of the atoms in space. This suggestion, in van't Hoff's own words, set him to thinking, and to such good purpose that the results of his thinking are now accepted, with some modifications, by most students of Organic Chemistry.

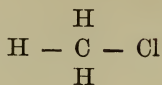
In van't Hoff's work, as is well known, the organic compound is symbolized by a tetrahedron, with the carbon atom situated in the centre, and the combining atoms or radicals in

the solid angles. It should be mentioned that the tetrahedral symbol was suggested by Kekulé as early as 1867, as representing well the quadrivalence of carbon, and the equal value of the four bonds. Before entering into the details of van't Hoff's work, it may be advantageous to review some simple cases in which the use of this symbol is shown to be an improvement over the ordinary structural formula representing the molecule in a plane, but it should be remembered that any molecular formula must be looked upon as a symbol expressive of thoroughly ascertained facts and not as a complete picture of the molecule, but that that symbol will be the best which illustrates the largest number of facts, and is out of harmony with none.

At the outset, *in adopting any definite symbol* we must assume that it is as essential that the atoms composing a molecule should arrange themselves in some definite position of equilibrium, depending on their affinity for each other, as that the planets of the solar system should retain their relative positions. [Without external force or some new disturbing influence, the relative positions can no more be changed in one case than in the other.] If, for example, we consider the molecule  $\text{CH}_4$ , it is but reasonable to suppose that the atoms will arrange themselves in such a way that all of the hydrogen atoms will be at the same distance from the carbon, and also that each hydrogen atom will be equidistant from all of the others. This condition of affairs is satisfied by the conception of the carbon atom situated in the centre of a tetrahedron which has a hydrogen atom in each of its four solid angles.

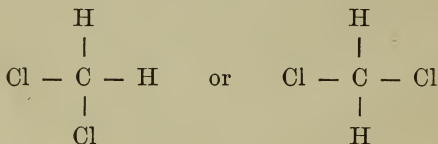
Again, consider the molecule  $\text{CH}_3\text{Cl}$ . There can be no reason for supposing that one hydrogen atom is differently situated in relation to the chlorine from the others, and there is nothing in the chemical behavior of the body to

suggest such an arrangement; yet this is exactly what is suggested by the ordinary plane formula, —



To show this body in a position of stable equilibrium we should, rather, picture the three hydrogen atoms all at equal distances from the carbon, and all at equal distances from the chlorine, and this condition of affairs would be perfectly represented by a tetrahedron with the carbon atom in the centre, and the hydrogen and chlorine in the solid angles.

As another illustration, suppose two of the hydrogen atoms in  $\text{CH}_4$  to be replaced by chlorine, giving  $\text{CH}_2\text{Cl}_2$ ; using the ordinary plane formulas, this could be represented in two ways: —

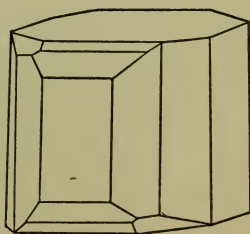
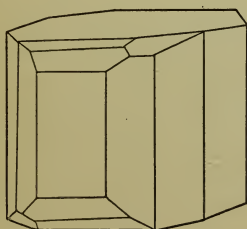


These two formulas should represent two different isomeric bodies, but no such isomerism has ever been observed. But if we consider the molecule as a system held in equilibrium by the mutual attraction and interaction of all of its parts, even the atoms which are not directly linked exerting some force of attraction, then it is plain that there will be only one position of the atoms in which they will be in a state of stable equilibrium, and that the arrangement will be a symmetrical one, corresponding again to the tetrahedral figure, with the hydrogen and chlorine atoms in the solid angles.

It is not, however, necessary to suppose that the form of

the molecule is always that of a *regular* tetrahedron, with the combining atoms or radicals fixed in the solid angles. Without at present discussing the question of oscillatory motions of the atoms in the molecule, the mean form assumed by a carbon atom with its four attendant radicals would probably be that of a regular tetrahedron, in case the four atoms or radicals were alike; but if different, some may be drawn nearer to, and others driven farther from, the carbon, thus forming irregular tetrahedrons.

The illustrations given above will perhaps suffice to show that the tetrahedral symbol of carbon is in more complete accordance with observed facts than the ordinary formulas in which the molecule is represented in a plane, but the principal use of the tetrahedral formula has been in explaining cases of physical isomerism. Such cases are too well known to need illustration, but the phenomenon is so well shown by the tartaric acids that a brief allusion to these must be pardoned. It is well known that ordinary tartaric acid is dextro-rotatory. Racemic acid, which resembles tartaric acid so closely that it must be assigned the same structural formula, differs from it in its crystalline form and optical properties, racemic acid being optically inactive. Now if this latter acid in the form of its sodium-ammonium salt be allowed to evaporate spontaneously, crystals of two kinds are developed, as shown in the following figures:—





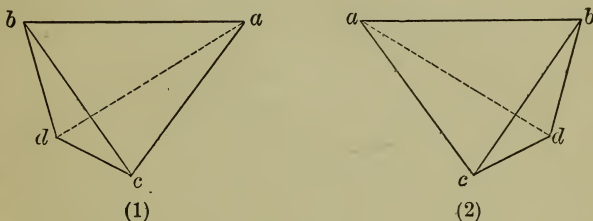
In each kind there is a hemihedral development, and each is the complementary form of the other, so that a crystal of one kind held before a mirror gives an image which is exactly like a crystal of the other kind. One of these kinds of crystals is found to be ordinary dextro-tartaric acid, while the oppositely developed crystals rotate the plane of polarization to the left, and are laevo-tartaric acid. Racemic acid is thus proved to be a mixture of two physical isomerides which rotate the plane of polarization equally in opposite directions; and in general it may be said that the existence of any optically active body implies the possible existence of another which will rotate the plane of polarization in the opposite direction, and which, if the bodies crystallize, will be an enantiomorphous form.

It has, of course, been long known that many *crystalline* bodies rotate the plane of polarization of light; but the peculiarity in the case of the active organic bodies is that their *solutions* have this power, and in some cases it has also been observed when the substance was in the state of vapor. The phenomenon in these cases, then, must be ascribed to some property inherent *in the molecule*. In crystals this optical activity has long been attributed to a certain lack of symmetry in the arrangement of the molecules of the crystal, since it has been observed only in bodies which show a hemihedral or tetartohedral development, and which occur in enantiomorphous forms. It is natural to infer that optical activity would in all cases be produced by similar causes. It follows, then, that in those organic compounds which are optically active, there must be a lack of symmetry inside the molecule itself. Now, going back to the tetrahedral symbol, if we have an asymmetric carbon atom, — that is, a carbon atom joined to four different atoms or radicals, — we have a



tetrahedron which has no plane of symmetry. In such a case as this, and only in such a case, is it possible, still using the tetrahedral symbol, for the atoms to have two different positions with regard to the carbon, the relation between the two figures being that of an object and its reflected image, or that between two enantiomorphous crystalline forms.

In the accompanying figures, in relation to the carbon atom situated at the centre, the order  $abc$  in (1) is to the right, and in (2) to the left, and any three of the groups will be found similarly to lie in reverse orders in the two forms.



We thus carry over into the molecule the idea of right-handed and left-handed forms similar to the forms which have been observed in crystals which have a similar effect on polarized light. The bodies are non-superposable. Their close similarity, their identity of atomic linking, forbids that there should be any difference in their behavior toward reagents, but allows slight physical differences, prominent among these being that if one rotates the plane of polarization to the right, its enantiomorphous form must rotate it to a corresponding degree to the left. According to this, the existence of a dextro-rotatory body always implies the possible existence of a laevo-rotatory. The central pivot, then, of the van't Hoff-Le Bel hypothesis, is that every optically active body contains an asymmetric carbon atom.

It should be noted that, though this is spoken of as the van't Hoff-Le Bel hypothesis, the subject has been approached thus far rather from the standpoint of van't Hoff, than from that of Le Bel. The latter, whose original paper<sup>1</sup> appeared in September, 1874, two months before that of van't Hoff, bases his reasoning upon the work of Pasteur and others, who had completely established the correlation existing between molecular dissymmetry and rotatory power. He concludes that in any body of the type  $MA_4$ , if three of the atoms or radicals be replaced by three different atoms or radicals, the result will be an unsymmetrical body, and this will possess rotatory power provided the four radicals have fixed position and are not in one plane. He therefore makes his statement the converse of van't Hoff's, but agrees with the latter in connecting optical activity, in general, with the presence of asymmetric carbon, though his reasoning is entirely independent of any hypothesis in regard to the tetrahedral form. In a later paper<sup>2</sup> he says, "The reason which led me to give to my demonstrations a particular and less simple form was that I had doubts as to whether  $CR_4$  had really the form of a regular tetrahedron or not," these doubts being based upon the observed crystalline form of some bodies of the  $CR_4$  type.

The next question that naturally arises is, how has the van't Hoff-Le Bel hypothesis been borne out by facts? At first, succinic acid, styrol, and a number of other compounds were cited as bodies which were optically active and yet contained no asymmetric carbon, but by careful experiments it has been found that if these substances are perfectly pure, they are entirely inactive, and at present no optically active

<sup>1</sup> Bull. Soc. Chem. (2) 22,337.

<sup>2</sup> Bull. Soc. Chem. (3) 3-788.

organic compound has been discovered whose formula does not contain an asymmetric carbon atom. Further, the derivatives of an optically active body are sometimes active and sometimes inactive. In all cases in which the activity is destroyed, the carbon atom loses its asymmetry; in all other cases the formula still contains asymmetric carbon.

It is to be noticed that the converse does not necessarily hold good; namely, that every substance containing an asymmetric carbon shows optical activity. Many bodies are known whose formulas contain asymmetric carbon, and yet in which no optical activity has been observed. In some cases we cannot assign any definite cause for the lack of activity. It may be that the rotatory power is so feeble as to elude detection, or that the body is not sufficiently soluble to show the phenomenon; but in many cases this inactivity can be easily explained. In some chemical reactions there is nothing to determine whether the right or the left handed body shall be formed; one can be prepared as readily as the other. In such a case, the chances are that just as many molecules of one will be formed as the other, and the result will be a mixture of two equally but oppositely active bodies, which will therefore be inactive. Referring to the illustration given above, racemic acid seems to be a mixture of dextro and laevo tartaric acids.

It is an interesting fact that when a compound with an asymmetric carbon atom is produced in a vegetable or animal organism, it is found almost without exception to possess optical activity, whereas when the same compound is formed artificially, the optical activity is generally wanting. In the latter case it is probable that equal quantities of the right and left handed modifications are formed, producing inactivity, but living organisms have a tendency to destroy one

of the modifications, so only one form, and that active, is produced by their agency.

Many inactive bodies have been proved to be mixtures of their dextro and laevo-isomers, and by the process called mesotomism have been separated into their active components. At the present time, no inactive body containing only one asymmetric carbon atom has withstood mesotomism, and on the other hand, no inactive body which does not contain asymmetric carbon has been found capable of mesotomism.

The methods used to bring about this separation are principally:—

1. Pasteur's process, which consists in the use of micro-organisms.

These have unequal aptitudes for destruction of the two isomers, and, in many cases, their growth, if carried on long enough, destroys one and leaves the other active component of the inactive body.

2. The method based on unequal aptitude of the two active isomers to combine with a compound possessed of rotatory power. Thus an active base is added to separate the constituents of an acid, or an active acid to separate the constituents of a base. If inactive malic acid, for example, is half neutralized by the active base cinchonine and allowed to crystallize in presence of active malate of cinchonine, the active malate is separated out.

3. The method of crystallization in hemihedral, enantiomorphous forms, already illustrated in the formation of the two active tartaric acids by the crystallization of the sodium-ammonium salt of racemic acid. This method can be used only in very rare cases, since few of the organic bodies show a sufficient tendency to perfect crystallization.

The *second* method given is evidently applicable only to

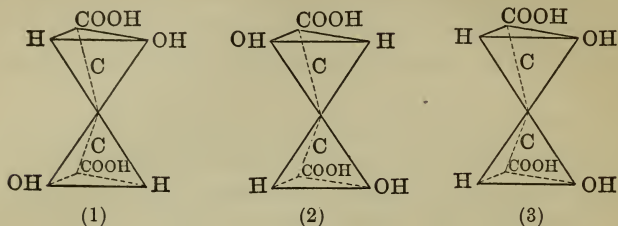
acids and bases, therefore the method by use of micro-organisms is the most general of the three. This was the first one used, and since it was for some time the only way known for producing optically active bodies, it gave rise to the belief that such bodies could only be produced by the agency of life.

Since the number of inactive mixtures is large, and the methods for separating them few, it is not strange that there are still many such bodies from which no active isomers have been obtained. This, however, offers no proof that they are not really mixtures of active components, and the number of bodies proved to be such mixtures is constantly increasing.

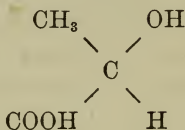
It has been suggested by Victor Meyer that these mesotomic bodies, instead of being mixtures, may be polymeric forms of the active constituents. In that case, they would seem to be connected very closely with the bodies next to be mentioned, — the *amesotomic* inactive bodies, containing asymmetric carbon, but having a symmetrical formula. In these cases there are at least two asymmetric carbon atoms, and the two halves of the molecule are exactly alike, so that we may conceive of the atoms as arranged around one of the asymmetric carbons in such a way as to rotate a beam of light to the right, and arranged around the other in the reverse order so as to rotate it equally to the left. The conditions, then, are similar to those of the mesotomic type mentioned above, except that the mixture is inside the molecule, and the constituents cannot be separated from one another without breaking up the molecule. As an illustration of an inactive amesotomic body, we have inactive tartaric acid, which differs from racemic acid in that it cannot be separated into the dextro and laevo-acids. Thus, in the following formulas if



(1) represents dextro-tartaric acid, laevo-tartaric acid will be represented by (2), and the inactive modification by (3).



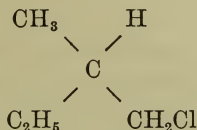
The mere presence of an asymmetric carbon atom does not seem to be sufficient of itself to produce an appreciable rotatory power. A certain amount of complexity in the molecule seems also to be necessary, sarco-lactic acid,



being the simplest substance which in the liquid state rotates the plane of polarization. Of substances containing less than three carbon atoms, not one has been proven active, though many contain asymmetric carbon. Perhaps some connection may be traced between this fact and the work of Philippe A. Guye,<sup>1</sup> who has (recently) endeavored to prove that the amount of rotatory power depends somewhat on the specific gravity of the radicals connected with the asymmetric carbon. He states that if we have two bodies  $CR_1 R_2 R_3 R_4$ , and in one the specific gravities are —  $R_1 = 100$ ,  $R_2 = 101$ ,  $R_3 = 102$ , and  $R_4 = 103$ , and in the other  $R_1 = 10$ ,  $R_2 = 100$ ,  $R_3 = 1000$ ,

<sup>1</sup> Annales de Chim. et de Phys. 6, xxv. 145.

and  $R_4 = 10,000$ , the lack of symmetry will be much greater in the second case than in the first, and there should be a corresponding difference in the amount of optical activity. This idea seems not to be entirely without experimental verification, for M. Le Bel has found that the angle for amyl chloride,

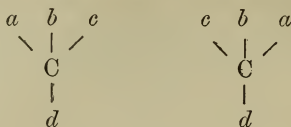


is  $1^\circ 6'$ ; for amyl bromide is  $4^\circ 24'$ ; and for amyl iodide  $8^\circ 20'$ . Moreover, Guye has studied 43 bodies derived from amyl chloride by replacing the  $\text{CH}_2\text{Cl}$  by radicals, in which the mass of the replacing radical is, as is the case with  $\text{CH}_2\text{Cl}$ , greater than that of the other three groups combined with the asymmetric carbon, and finds that they are all, like amyl chloride itself, dextro-rotatory, his object being to show that the *direction* as well as the *amount* of optical activity depends upon specific gravity. Now it may be that in the simpler molecules containing less than three carbon atoms, there is not sufficient difference in the specific gravities of the radicals to cause appreciable optical activity.

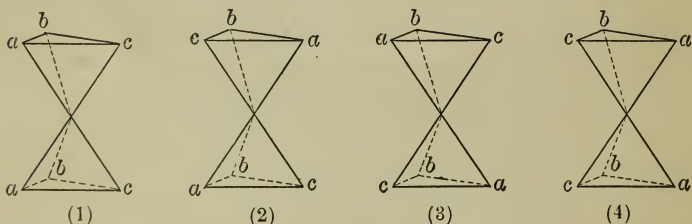
Victor Meyer's explanation of the lack of observed rotatory power in the more simple molecules containing asymmetric carbon, is that the simple groups are more mobile than the complex ones, and may keep changing their positions in the molecules, thus producing a tautomerism incompatible with the display of optical activity, the result being the same as if we were dealing with mixtures of opposite molecules.

The number of isomeric forms possible for any particular combination of atoms depends upon the number of asym-

metric carbon atoms which it contains. For C (*abcd*), as we have seen, we may have the two geometrical forms, —



one of which will be dextro and the other laevo-rotatory. If, however, in these formulas *d* represents another asymmetric carbon atom with its attendant radicals, two different positions are also possible for this group, making four possible isomers with two asymmetric carbon atoms. In general,  $N = 2^n$ , in which  $N$  = the number of isomers and  $n$  = the number of asymmetric carbon atoms. If, however, *d* = another asymmetric carbon exactly like the first, so that we have the symmetrical molecule  $C_2(abc)_2$  the case is somewhat different. The four possible configurations then become: —



Of these, (1) and (4) evidently represent the same body, (4) being (1) inverted, so that in this case the possible number of isomers is reduced to three. In general, if there are  $n$  asymmetric carbon atoms in a *symmetrical* formula, there are theoretically possible  $\frac{1}{2} 2^n$  *active* isomers grouped in pairs having equal and opposite rotatory power and enantiomorphous crystalline form, and  $\frac{1}{2} 2^n$  representatives of the inactive



amesotomic type. It is true that for most substances the number of isomers found does not come up to the number predicted by this rule. For example, theory demands sixteen bodies of formula  $C_6H_{12}O_6$ , whereas only fourteen<sup>1</sup> have been observed. In the case of the tartaric acids, however, which contain two asymmetric carbon atoms in a symmetrical formula, all of the bodies theoretically possible have been obtained.

It has been noticed that an optically active body sometimes loses its rotatory power simply upon heating. Racemic acid, for example, can be made by heating ordinary dextro-tartaric acid. This seems to be due to the partial change by heat into the oppositely active body which neutralizes the rotatory power of the body with which we started, or it may be that the mobility of the atoms, of which Victor Meyer speaks, may be increased by the heat, producing tautomerism.

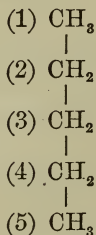
Two singly linked carbon atoms, according to van't Hoff, should be represented by two tetrahedrons having the carbon atoms at the same time at the centre of one and the solid angle of the other tetrahedron. This would give the figure of two truncated pyramids having the plane of truncation in common, but for ordinary purposes of representation it is generally considered sufficient to have the two tetrahedrons with a solid angle in common, as has been shown in the preceding illustrations.

It can readily be seen, and is shown very plainly with tetrahedral models, that several singly linked carbon atoms will lie in a zigzag line, or a ring, this depending upon the angle which the axes of attraction or tetrahedral axes make with each other. This angle is  $109^\circ 28'$ , which is very nearly the same as the angle of the regular pentagon,  $108^\circ$ ;

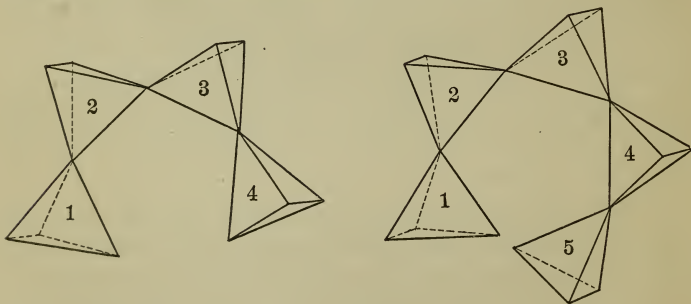
<sup>1</sup> Am. Chem. J. 13, 64.

therefore five such atoms could readily form a closed ring, and only a slight deviation of the axes from their normal direction would be necessary in order to produce a ring of six atoms,—a consideration which may perhaps account for the great stability of five and six atom carbon rings.

The formula for normal pentane, as generally written,



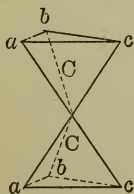
gives an incorrect idea of the molecule in so far as it indicates that (1) must be nearer (3) than (4) or (5). Applying the tetrahedral theory, the formulas for butane and pentane may be represented as follows:—



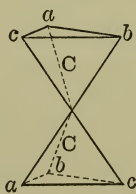
In "Die Lagerung der Atome im Raume," van't Hoff starts out with this statement: "The present chemical theory has two weak points. It takes into consideration neither the

relative positions which the atoms assume in the molecule, nor their kinds of motion." Thus far we have been occupied principally with the subject of the relative positions, and the next step in advance will be to consider what this theory supposes in regard to the *motions* of the atoms. In the first place, it must be conceded that any atomic motions in the molecule must be limited in such a way that the atoms will, in general, keep fixed relative positions; otherwise isomerism would be an impossibility.

In considering the motion inside the molecule, van't Hoff starts with the assumption that any such motion must be regular and periodic to account for the constancy of properties of the particular substance. In the case of two singly linked carbon atoms, one of the simplest conceivable motions is a rotation around the axis joining the carbon atoms. If the rotation of both atoms is in the same direction, it becomes practically a motion of the molecule as a whole, but it is assumed that the two carbon atoms may rotate in opposite directions at the same time, thus producing configurations such as would result if one of the carbon atoms was in rotation while the other was at rest. Van't Hoff's first assumption was that such a rotation was continually taking place, and that, therefore, the two following formulas,

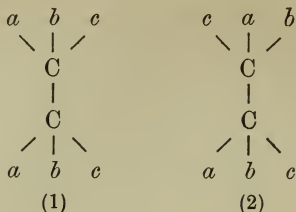


(1)



(2)

or, more simply,



should be considered as representing the same body in different phases of rotation rather than two different bodies, since (2) can be derived from (1) by simple rotation of the upper carbon atom to the right.

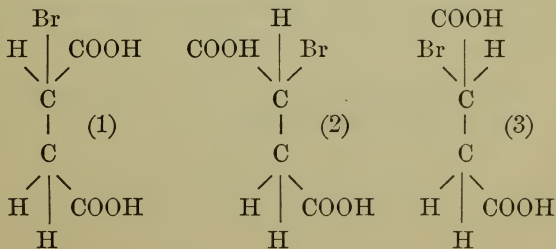
If we deny the possibility of such rotation, and consider each possible configuration of the atoms as a distinct isomeric form, we are led to possibilities of isomerism which are practically infinite. For example, in the very simple formula  $\text{CH}_3\text{-CH}_3$ , the three hydrogen atoms of each group might lie in the same vertical lines with the three of the other group, or midway between these positions, or there is a possibility of any number of arrangements between these two, so that if we consider each of these possible arrangements as representing a distinct isomeric form, the number of such possible forms reaches alarming proportions. These difficulties vanish, however, if we assume free rotation, and accept an hypothesis sometimes referred to as "Van't Hoff's second hypothesis." This is as follows:—

"When two atoms of carbon are united by a single bond, each is capable of free rotation in either direction about the common axis; and isomers may be recognized for those bodies only which cannot be brought into the same configuration by such rotation."

In van't Hoff's later works he states, however, that in all probability there will be one arrangement of the atoms in the

molecule which will possess the greatest possible stability, and this will be the arrangement which the atoms will tend to assume when the molecule is in a state of equilibrium. It is Wislicenus's idea that, if the radicals connected with two singly linked carbon atoms are all alike, rotation will be started by the slightest impulses of heat, since there will be no one position which will be more stable than another, and therefore nothing to determine a fixed position of equilibrium. If, on the other hand, the radicals are different, their chemical affinities will come into play. The atoms or radicals not directly combined in the molecule exert chemical attraction upon one another, the two with greatest affinity tending to come as near together as possible, thus determining a position of equilibrium at which the rotation will cease, or tend to cease. It is evident that more force would be required to produce rotation in such a system, held in a definite position by the mutual attraction of the parts, but it is probable that at sufficiently high temperature there are always some configurations in a molecular aggregate which do not correspond to the greatest attraction. This number will increase with the rising mean temperature of the mass, but even at high temperatures the most stable molecules will predominate.

These ideas may perhaps be made more plain by an illustration. The three formulas,



according to van't Hoff's second hypothesis, represent the same molecule in different phases of rotation rather than three isomeric modifications, since each can be derived from the preceding by simple rotation of the upper carbon atom to the right; (3) would, however, probably represent the most stable form, the configuration which would be assumed in the largest number of molecules, because here the negative radicals COOH and Br, joined to one carbon atom, lie as near as possible to the hydrogen of the other carbon atom; that is, they are in the same vertical line.

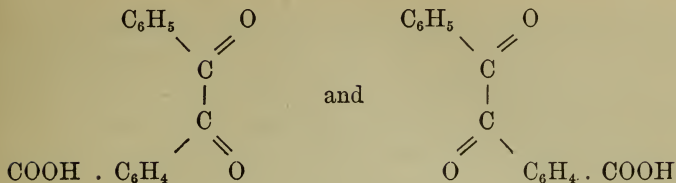
Recently there has been some discussion as to whether such rotation is *always* possible, or whether it is dependent on certain conditions. The idea of *limited* rotation was first suggested by V. Meyer in connection with the oximes, which will be discussed later when we consider the stereo-chemistry of nitrogen. Later Bethmann<sup>1</sup> decided that, in order to explain the isomerism in succinic and glutaric acids, he must deny free rotation in those molecules, and concluded that the carbon bound to *carboxyl* cannot rotate freely, but stops in certain definite positions, and these different positions correspond to different isomeric modifications. Perhaps one of the best illustrations of alleged limited rotation may be found in the benzil monocarbonic acids. Graebe,<sup>2</sup> and Meyer,<sup>3</sup> working later with other experiments, proved that there are two of these acids differing very slightly in chemical as well as physical properties, and to these two bodies they ascribe the formulas: —

<sup>1</sup> Zeit. f. phys. Chem. 5, 385.

<sup>3</sup> Ber. 23, 2079.

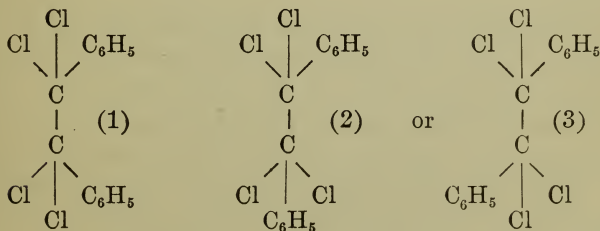
<sup>2</sup> Ber. 21, 2003, and Ber. 23, 1344.





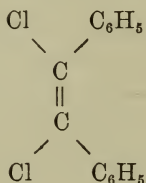
In case free rotation were possible, these formulas, according to van't Hoff, should represent one and the same body instead of two different ones. Meyer's final conclusion is that in the great majority of cases we should assume free rotation, for the difference in character of the constituents will bespeak a certain position of equilibrium, and rotation will take place until this position is reached; but in those cases in which the radicals or atoms stand very near each other in electrical character, a state of equilibrium may be reached in several different ways, and so several different stable bodies may be formed.

Eilhart<sup>1</sup> has endeavored to show that the rotation depends on the temperature much as dissociation does. To do this he discusses the case of tolane tetrachloride, which may be represented by the following formulas:—

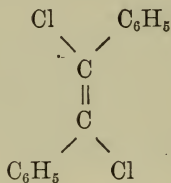


<sup>1</sup> Guide to Stereo-Chemistry, p. 24.

These, according to van't Hoff, represent one and the same body; but (2) and (3) are the more stable configurations which we should expect the atoms to assume. If put with zinc, we should expect the two adjacent chlorine atoms to be extracted; that is, the two chlorine atoms lying in the same vertical line in the formula, and the remaining atoms to retain their original relative positions. According to this, (1) would yield the *unstable* dichloride having the formula:



and (2) and (3) would each yield the stable dichloride, having the formula:

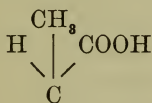


This experiment has been done quantitatively, and at 80°, one-third of the reduction yield consists of the *unstable* dichloride and two-thirds of the *stable* dichloride, which would seem to indicate that at that temperature free rotation was taking place and molecules of all three kinds were present. At 20°, however, considerably more than two-thirds of the reduction yield consists of the *stable* dichloride, showing that, at the lower temperature, the directive affinities come into play to stop the rotation at places of stable equilibrium.

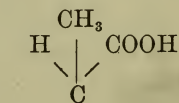


The question then arises, can we predict just what the arrangement of the atoms inside the molecule will be when they have assumed the position of stable equilibrium? In some cases it seems comparatively easy. In the tolane tetrachlorides given above, it seems reasonable to suppose that the  $C_6H_5$  and Cl will tend to draw as near together as possible, and therefore that the position of stability is assumed when these are in the same vertical line. In many cases, however, there is more difficulty. Wislicenus assumed that the greater the difference in positivity of two radicals not directly united, the greater their mutual attraction. Baeyer puts this in a different form, which in some cases would coincide with Wislicenus's view, but in others it would not. He assumes that the attraction corresponds to what would exist between the two radicals if they were directly connected.

He was led to this difference from Wislicenus by a study of the methyl-succinic acids, for which Wislicenus gave the following formulas: —



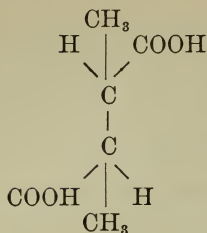
and



(Active.)

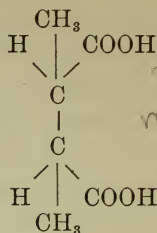
(Inactive.)

But these formulas do not show why the inactive acid should form its anhydride more readily than the active, nor are they in agreement with the stability of the anhydrides. Baeyer, therefore, suggests as formulas for the two acids, —



(Active.)

and

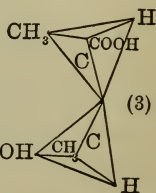
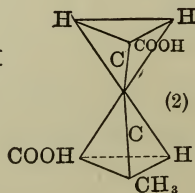
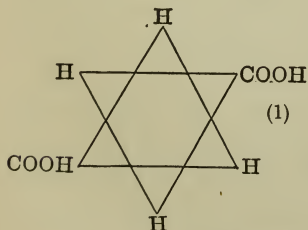


(Inactive.)

*This agrees  
w. i. Tard*

assuming that methyl has a stronger attraction for methyl than for carboxyl, on the principle that methyl is held more strongly to methyl in ethane than to carboxyl in acetic acid. But to determine the strength with which groups are held together in a molecule is not always an easy task.]

Bethmann<sup>1</sup> has determined the affinity constants of some organic acids by measuring their electrical conductivity, and has proved that this constant in a dibasic acid increases as the distance between the carboxyl groups diminishes. Now since methyl succinic acid has a larger affinity constant than succinic acid, it may be inferred that the introduction of methyl draws the carboxyls nearer together. Dimethyl succinic acid has a still larger affinity-constant, therefore the addition of another methyl group seems to draw the carboxyls still nearer together. Bethmann explains these facts by the following formulas:—



<sup>1</sup> Zeitschrift für Phys. Chemie, 5, 385.

In (1), the molecule is supposed to be viewed from above, and one tetrahedron is turned half way around, so that the carboxyl of one tetrahedron lies halfway between the two hydrogen atoms of the other. When methyl is introduced, the attraction of methyl for carboxyl draws the tetrahedron around until the methyl and carboxyl are in "corresponding" positions. By the addition of another methyl, the tetrahedrons are supposed to be drawn over towards each other so that the methyl and carboxyl are much nearer each other than the two hydrogen atoms.

Bethmann's general hypothesis is, however, not found to hold good in all cases, though apparently tenable for the succinic acids quoted, since in these acids the greater nearness of the carboxyls with increasing number of methyl groups has also been proved by Bischoff<sup>1</sup> in another way. It is naturally assumed that the ease of formation of anhydrides will increase as the distance between the carboxyls grows less. Now Bischoff has found that while succinic acid is dehydrated only with the greatest difficulty, the ease of dehydration increases directly with the number of methyl groups, tetramethyl succinic acid forming its anhydride most easily. The general idea of the approaching of the carboxyl groups as methyl is added is thus confirmed, but Bischoff's formulas to express and explain these facts differ from those of Bethmann. The former holds that the state of equilibrium of a molecule is best expressed by assuming that the radicals are as far apart as possible instead of as near together. This can best be represented on a plane surface, by supposing that the molecule is viewed from above, giving the figure of a six-rayed star, as in Bethmann's formula for succinic acid above. Bischoff farther holds that methyl and carboxyl have a *repul-*

<sup>1</sup> Ber. 23, 620, and 3419.

sion for one another, and it is this repulsion which drives the carboxyls nearer together.

In regard to the attractions and repulsions of methyl and carboxyl, Bischoff formulates the following rules:—

I. Carboxyl is repelled by carboxyl. In this he agrees with Wislicenus.

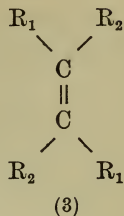
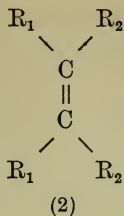
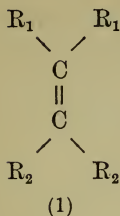
II. Methyl is only slightly repelled by methyl. Von Baeyer states that these radicals attract, and Wislicenus that they repel one another.

III. Carboxyl is repelled by methyl. This is in direct opposition to Wislicenus.

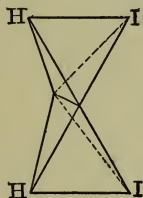
This diversity of opinion in regard to the attractions and repulsions of the most common organic radicals shows that this branch of the subject is still in a very unsettled state. In the simpler cases, it is possible to fix upon the exact arrangement of the atoms in the molecule, when in a state of stable equilibrium, with a fair degree of probability, but in many cases this is impossible.

In the case of compounds containing doubly linked carbon atoms, isomerism has also been observed which can be explained most readily on the supposition of the carbon atom as situated in the centre of a tetrahedron, but in this case the isomerism does not manifest itself by optical activity, and we have no longer to deal with the asymmetric carbon atom.

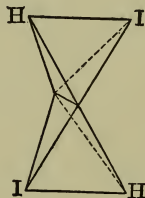
Two carbon atoms, joined by double bonds, must, in the terms of <sup>Hofmann's</sup> our theory, be represented by two tetrahedrons having two solid angles, or an edge, in common. The four atoms joined to the two carbons will then lie in a plane. In the formula  $C_2(R)_4$  there will of course be no possibility of isomerism, and the same may be said of  $C_2(R_1)_3R_2$ . With  $C_2(R_1)_2(R_2)_2$ , however, there are three possible arrangements:—



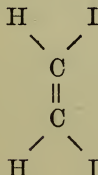
(1) is immediately recognized as essentially different from (2) and (3), but the tetrahedral theory is called into play to account for the differences between (2) and (3). As a particular instance of this kind we may cite  $C_2H_2I_2$ . Two bodies are known having the formula  $CHI = CHI$ , differing in volatility, melting point, and specific gravity. These bodies could not be explained upon any former theories, but can be readily explained on the present hypothesis, being represented by the formulas:—



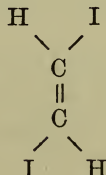
and



or,

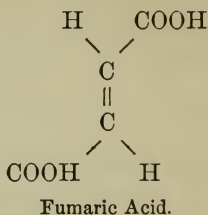
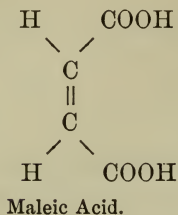


and

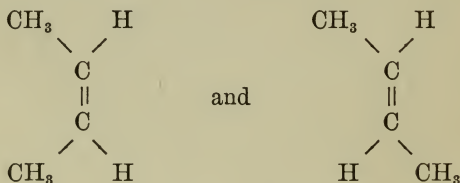


Another illustration of this kind of isomerism is found in maleic and fumaric acids, which have long been known as *were formerly*

bodies whose isomerism was inexplicable. This isomerism is now explained by giving them the formulas,



Many cases of this kind of isomerism are well known. There are many other bodies, however, whose formulas admit of this kind of isomerism, in which the phenomenon has not been observed. Butylene, for example, is known with certainty only in one form, although we might expect two modifications represented by the formulas,



and there are some reasons for supposing that two such bodies really exist.

It can readily be seen that with  $\text{C}_2(\text{R}_1)_2\text{R}_2\text{R}_3$ , there will be three possible isomerides similar to those given above, and that with  $\text{C}_2(\text{R}_1\text{R}_2\text{R}_3\text{R}_4)$  the number of possible arrangements is increased to six.

It must be noticed that if we assume the possibility of free rotation as in the case of singly linked carbon atoms, then the formulas for maleic and fumaric acids as given above



would be identical. Now since isomerides have been observed, with slight differences in properties, which can only be explained by formulas similar to these, the van't Hoff theory denies the possibility of free rotation in the case of doubly linked carbon atoms. That free rotation is incompatible with double linking is well expressed to the eye by the tetrahedral symbols. If we have the two tetrahedrons with an edge in common, it is evident that one cannot be revolved about the axis joining the centres of the two tetrahedrons without disturbing this arrangement, or breaking the bonds which hold together the two atoms.

In such bodies, as has been stated, there is no optical activity, but the isomerides differ in most physical properties and also, to a slight extent, in chemical properties, as, for example, in the ease of formation of anhydrides, though these variations are not sufficient to demand a difference in atomic linking. In the case of singly linked carbon compounds just discussed, the differences in the isomerides are limited almost entirely to optical properties, although the divergence in other physical properties becomes somewhat greater as the number of asymmetric groups increases. These two kinds of isomerism, it will be noticed, are explained on the same general principle, but this explanation gives room for greater differences in properties in the second case than in the first, since the absolute distance of the atoms from each other is different in the two isomerides in which the carbon atoms are doubly linked, whereas, in the singly linked isomerides, the individual atoms and radicals have exactly the same position with reference to each other except for the difference of right and left, and the distance apart of any two individual radicals is the same in both cases. This answers the main objection of Michael and Claus, who have been the

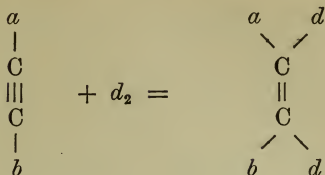


principal opponents of the Le Bel-van't Hoff theory, and who have urged that the constitution of bodies which differ only in one single optical property should not be explained in the same way as the constitution of bodies which have quite different chemical properties, and especially since the optical activity is found to depend upon external circumstances, such as the solvent employed, and the concentration of the solution.

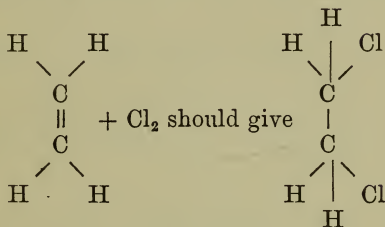
[Against some particular cases explained in a rather round-about way by Wislicenus, Michael may bring well-grounded arguments, but his objections are not weighty enough to shatter the fundamental basis of the van't Hoff-Le Bel theory. Michael himself regards many of these cases of isomerism as inexplicable on structural theories, but advances no explanation to take the place of the one which he rejects, merely giving a new name to such bodies and calling them alloisomeric.]

*looking  
same  
low,* In regard to *triply* linked carbon atoms, there is very little to be said. *Two* triply linked atoms must be represented by two tetrahedrons having three solid angles, or a *plane*, in common. The combining atoms or radicals must, then, lie in a straight line, and there is no chance for isomerism of any kind nor for any rotatory motion.

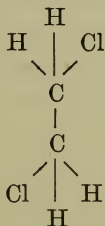
One of the ideas which Wislicenus first definitely formulated is that in the formation of addition products the atoms retain as nearly as possible the relative positions which they had originally; that is, atoms which, in the formula, lie in the same vertical line *before* the change will keep that relative position after the change. For example, taking a *general* illustration, —



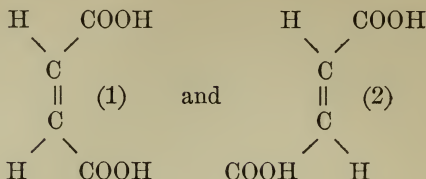
But in changing from double to single linkage these positions will not be permanent on account of the rotation which then becomes possible. For example, —



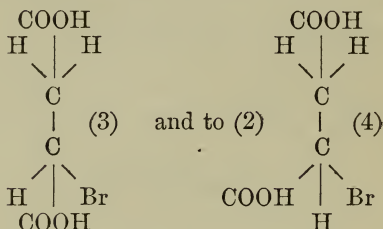
but now that the carbon atoms are singly linked, rotation of one of the carbon atoms is possible, and will proceed until the state of equilibrium is attained, represented by the following formula, —



Another good illustration of this may be found in the maleic and fumaric acids previously mentioned. They are represented respectively by the formulas, —

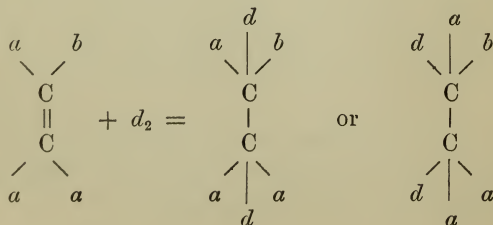


If we add H Br to (1) we should get, —



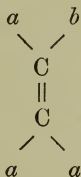
By rotation of the lower carbon atom in (3) we get an arrangement of atoms similar to that in (4), which is presumably a more stable form, and here we have an explanation of the well-known fact that both maleic and fumaric acids are converted by hydrobromic acid into monobrom-succinic acid.

In such cases as the latter, where there are two different radicals attached to one of the carbon atoms, Wislicenus points out the possibility of obtaining two geometrical isomerides. Thus, in general form, —

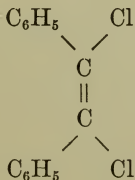


which are geometrical isomers. It would naturally be expected that both of these bodies should be formed at the same time in about equal quantities, and this explains why, in the formation of such addition products, one never obtains substances which rotate the plane of polarized light.

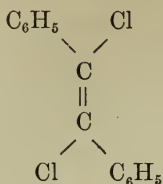
The above formulas also show that optically opposite modifications produce identical products if they go over into unsaturated compounds through the loss of the same radical. For example, if  $d_2$  be withdrawn from the geometrical isomers given above, the result will be one and the same body, —



Wislicenus also uses his principle of least disturbance in the formation of addition products, to determine the configuration of particular molecules. One or two simple illustrations of this may suffice at this point. Two tolane dichlorides are known. The one with the higher melting-point is obtained by the direct addition of chlorine to tolane, and must, therefore, be plane-symmetrical, having the formula,

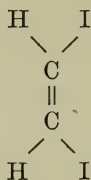


leaving the centre-symmetrical formula,

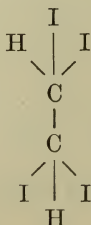


for the dichloride with lower melting-point.

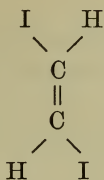
It would, in general, be expected that the body with centre-symmetrical formula should be more stable than its plane-symmetrical isomer, and this is found to be true in the cases where the configuration can be determined. Now two different iodo-ethylenes are found to result from adding iodine to acetylene. One is liquid and unstable, and the other solid and stable. Wislicenus concludes that the liquid body must be plane-symmetrical,



and must, therefore, be the one formed by the direct action of iodine on acetylene, while the other modification must be produced by a secondary reaction. To explain the simultaneous formation of this second modification, he assumes that a tetra-iodide is first formed,



and that  $I_2$  is given off to more acetylene, leaving the solid, stable, centre-symmetrical iodide,



Briefly summarized, we have shown in the foregoing that isomerism is of three kinds:—

1. Ordinary chemical isomerism, explained by difference of atomic linking.

2. Physical or optical isomerism. Differences limited almost entirely to difference in optical properties and crystalline form. The optical activity is due to the fact that the molecule possesses no plane of symmetry. The existence of an optically active body implies the existence of another equally but oppositely active, and the configuration of the molecules of these two bodies is such that they bear to each other the relation of an object and its image reflected in a mirror. Considering the four valencies of the carbon atom as extended in the directions of the four angles of a tetrahedron, the two optically active bodies may be represented by right and left tetrahedra.

3. Stereo-chemical isomerism. The amount of difference in properties lies midway between (1) and (2). There are differences in physical properties, and also to a slight extent in chemical properties, but not sufficient to indicate a difference in atomic linking. Found principally in connection with compounds containing two doubly linked carbon atoms. Explained on supposition of different arrangement in space of the radicals combined with the carbon atoms.

The principal suppositions concerning the carbon atom, which underlie the generally accepted stereo-chemical theories are as follows:—

1. The carbon atom possesses four equal valencies.

2. Observed facts are best explained by representing the carbon atom as situated in the centre of a tetrahedron with its four valencies extending in the directions of the four solid angles.

3. Two singly linked carbon atoms are <sup>generally</sup> represented as two tetrahedra having a solid angle in common; two doubly linked carbon atoms as two tetrahedra with an edge in common; and two triply linked carbon atoms as two tetrahedra with a face in common.

4. The motion of the atoms inside the molecule must be limited in extent, to account for isomerism; and of a periodic nature to account for constancy of properties.

5. In the case of two singly linked carbon atoms, the rotation of one atom with its attendant radicals around the axis joining the two atoms is considered possible, but except at high temperatures, this rotation ceases at some point determined by the chemical affinities of the radicals which are not directly connected.

6. In the case of doubly and triply linked carbon atoms, no rotation around an axis is possible.



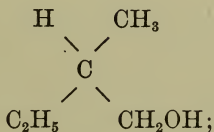
## II.

### ILLUSTRATIONS AND APPLICATIONS TO PARTICULAR CASES.

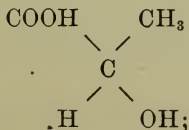
SINCE the value of any theory depends upon the number of facts with which it is found to be in harmony, it may be well, before taking up the more specialized part of this work, to consider the application of the general stereo-chemical theories to some well-known organic bodies. Such examples, it is to be hoped, will be of value in giving a clearer idea of the theories, and may at the same time enable us to see in how far these theories are in accordance with observed facts.

Among the more common substances in which optical activity has long been noticed may be mentioned the following substances, the formulas for which show that each contains an asymmetric carbon atom:—

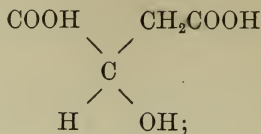
amyl alcohol,



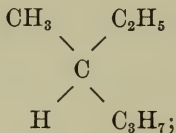
ethylidene lactic acid,



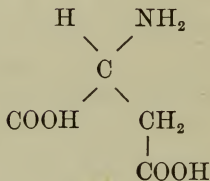
malic acid,



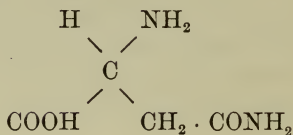
amylethane,



aspartic acid,



and asparagine,



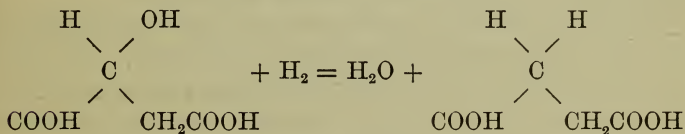
Two ethylidene lactic acids have long been known. Of these the fermentation lactic acid is inactive, and sarco-lactic acid is dextro-rotatory. In December, 1890,<sup>1</sup> by the action of a micro-organism on cane-sugar, an ethylidene lactic acid was obtained which was laevo-rotatory. We have, then, the two optically active bodies demanded by theory, and it only remained to prove that the fermentation or inactive acid is made up of these two active isomers,—a work which has

<sup>1</sup> Am. Chem. Journ. xiji. 277.

recently been accomplished. Inactive lactic has now been separated into its optically active components by three methods. Frankland and MacGregor<sup>1</sup> obtained sarco-lactic acid by the fermentation of inactive lactic acid, but found that if the fermentation was interrupted too early, the active was mixed with a large quantity of inactive acid, and if continued too long, the active lactate was also destroyed. Active components were also obtained from the inactive acid by crystallization of salts of the alkaloids, and finally Purdie<sup>2</sup> has found that the method of spontaneous resolution by crystallization can be applied with success.

The case of malic acid is very similar to that of lactic acid. Three different bodies are known, having the same structural formula; one is inactive, one is dextro-rotatory, and the other laevo-rotatory; and the inactive malic acid has been proved to be identical with that obtained by mixing equal quantities of the dextro and laevo acids.

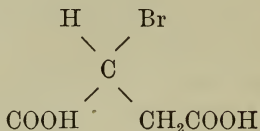
Active malic acid gives by reduction succinic acid, which is inactive. The reaction is expressed by the following equation:—



By this equation, the carbon atom is shown to have lost its asymmetry at the same time that the body loses its activity. On the other hand, right malic acid is produced by the reduction of right tartaric acid, in this case the resulting body as well as the original one containing asymmetric carbon.

The sugars have already been mentioned as optically active bodies containing asymmetric carbon, and with them belong the mannite and saccharic acid groups. In these latter bodies, there are four asymmetric carbon atoms and a symmetrical arrangement, so that theory predicts that, for each formula, there should be eight active and two inactive bodies. Of the ten theoretically possible bodies of formula  $C_4H_4(OH)_4(COOH)_2$ , eight have already been obtained.

Such illustrations as these might be almost indefinitely extended, but it should be noticed again that the mere fact that the resulting body contains asymmetric carbon does not necessarily imply that it will be active. For example, Kekulé obtained by action of hydrobromic acid on active malic acid, monobromsuccinic acid, which is inactive, though its formula



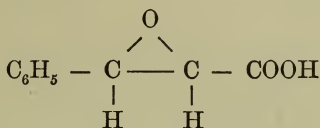
shows that it contains an asymmetric carbon atom.

It should perhaps be mentioned here that optical activity has been rarely observed in halogen derivatives. This has been so noticeable that some investigators have concluded that the presence of a halogen element is incompatible with optical activity. This, however, has been proved not to be absolutely the case, since Le Bel has discovered rotatory power in amyl iodide, and Guye in the corresponding bromide and chloride.

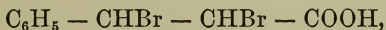
Phenyl-brom-lactic acid<sup>1</sup> has also been recently converted by cinchonine into a right and left handed modification, but

<sup>1</sup> Lieb. Ann. d. Chem. 271, 159.

in this case the optical activity may be due to the asymmetry of the carbon atom not directly connected with bromine. Erlenmeyer has also transformed this latter body into active phenyl-oxacrylic acid, which is interesting from the fact that in this case the two asymmetric carbons are, according to Glaser's formula, in a ring,



L. Meyer, jun.,<sup>1</sup> and C. Liebermann<sup>2</sup> have succeeded in decomposing cinnamic acid dibromide



by strychnine into two active isomers; and in this case it is evident that the activity must be due to the asymmetry of a carbon atom directly united with a halogen element. Recently, also, Walden<sup>3</sup> has shown that active chloresuccinic acid can be produced from active malic acid; so that although many efforts to prepare active asymmetric halogen compounds have met with failure, enough such compounds have been produced to show that the presence of a halogen is not absolutely fatal to optical activity.

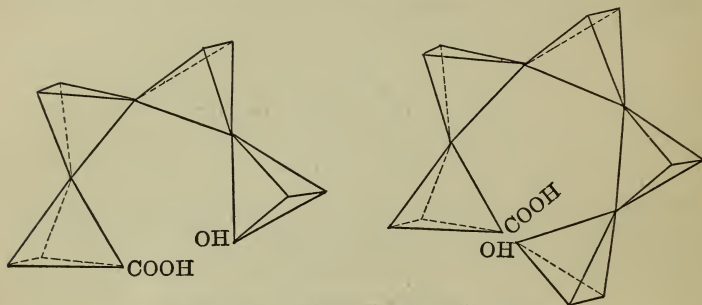
Certain reactions have been observed which result in the splitting off from a molecule of atoms apparently quite remote from each other. For example, lactones are formed by the splitting off of water from a carboxyl and hydroxyl group which are in the  $\gamma$  or  $\delta$  position relatively to each other rather than in the  $\alpha$  position as might be expected from the

<sup>1</sup> Ber. 25, 3121.

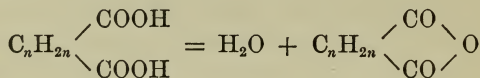
<sup>2</sup> Ber. 26, 245.

<sup>3</sup> Ber. 26, 210.

ordinary plane formulas. The use of the tetrahedral figures, however, as given below, explains this readily, showing that the hydroxyl and carboxyl groups may be much nearer each other when in the  $\gamma$  or  $\delta$  position than they could be in the  $\alpha$  or  $\beta$ .

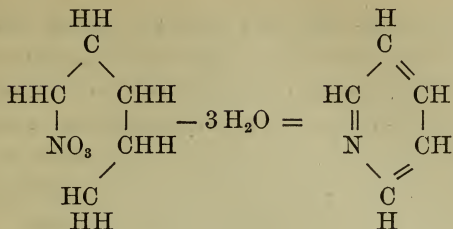


Another illustration of this same kind may be found in the fact that the  $\alpha$  and  $\beta$  amido acids do not lose water spontaneously, but the  $\gamma$  and  $\delta$  acids do so easily. The same explanation may also be applied to the fact that the reaction expressed by the following equation

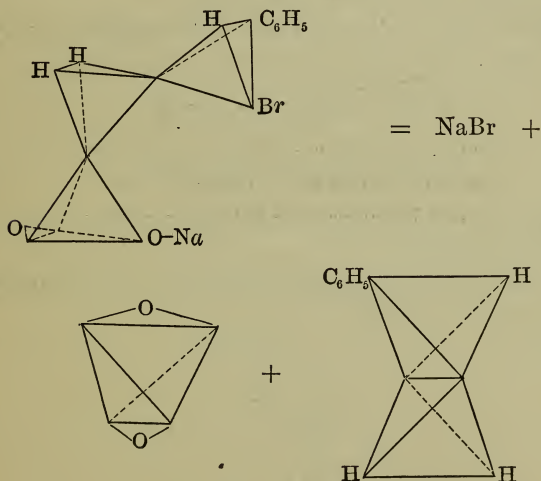


does not take place with oxalic or malonic acids, but only with succinic and glutaric acids; that is, in those acids in which the two carboxyl groups are in the  $\gamma$  and  $\delta$  positions relatively to each other.

This idea of the singly linked carbon atoms being arranged in a ring rather than in a straight line, is also in best agreement with the fact that amyl nitrate is converted by  $\text{P}_2\text{O}_5$  into pyridin, as is shown by the following equation, —



In compounds where NaBr and  $\text{CO}_2$  split off from the same molecule, it has been found that the sodium and bromine occupy the  $\beta$  position relatively to each other rather than the  $\alpha$ . A geometrically expressed equation shows the cause of this:—



On account of the affinity between the sodium and the bromine, they tend to bend the tetrahedrons from their original position until they get near enough so that these atoms split off.

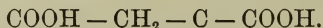
When we attempt to apply our theories to doubly linked



carbon compounds, the case becomes rather more complicated, because we have here bodies differing from each other in a number of physical properties, such as boiling and melting points, crystalline form, etc., and also to a slight extent in chemical properties, so that in many cases the question arises as to whether such bodies should be considered as geometrical isomers or structurally different bodies.

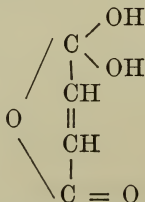
Among the most common of such cases of isomerism, which have aroused much discussion as to the cause, is that of maleic and fumaric acids.<sup>1</sup> It was at one time suggested that one of these acids was a polymeric form of the other, but on experiment their vapor densities were found to be identical, which gave the death-blow to that theory.

The Kolbe-Fittig explanation was that in maleic acid there was a divalent carbon atom, according to the formula,



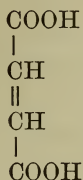
Such an explanation as this would seem to demand the possibility of a similar isomerism in ethylene itself, and all of its derivatives,—an isomerism which it is needless to say has not yet been observed.

Another explanation is given by Anschütz, who has assigned to maleic acid the formula,



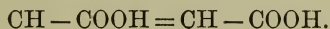
<sup>1</sup> Ann. Chem. Pharm. 246, 53. Bull. Soc. Chim. (2) 37, 300. Am. Chem. Journ. 9, 253 & 364. Michael, — Untersuchungen ueber Alloisomerie. Wislicénus, — Ueber die Räumlichen Anordnung der Atome in Organischen Molekülen, &c.

giving only to fumaric acid the formula

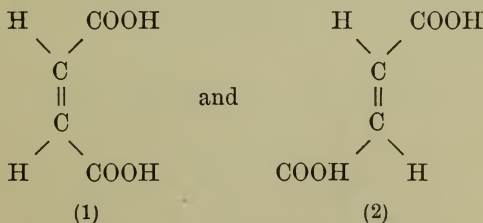


These formulas are in agreement with facts in so far as they would indicate that the maleic acid was less stable than its isomer, and readily formed its anhydride; but this explanation could only be applied to *acids* of this type, whereas a similar isomerism has been observed in a number of other cases, and there should therefore be a more general explanation.

The general consensus of opinion has assigned to these two acids the same structural formula,



According to the van't Hoff hypothesis, the atoms situated in the angles of two tetrahedrons, having two solid angles in common, admit of two arrangements, as,

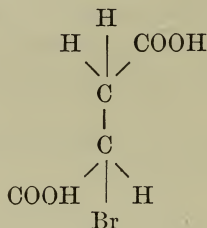


Of these (1) has been assumed to be the arrangement in maleic acid, as indicating the less favorable configuration for

stability, — and maleic acid is well known to be less stable than fumaric, — and also explaining the fact that maleic anhydride can be readily formed, whereas a similar reaction is impossible in the case of fumaric acid.

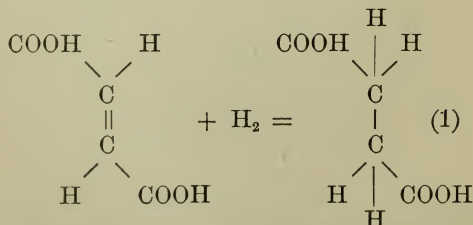
There are certain reactions of these bodies which seem especially well adapted to illustrate the theories given in the preceding chapter, and they will therefore be briefly noticed here.

Fumaric acid may be made by treating bromsuccinic acid with alcoholic potash. The most favorable configuration for bromsuccinic acid is, —

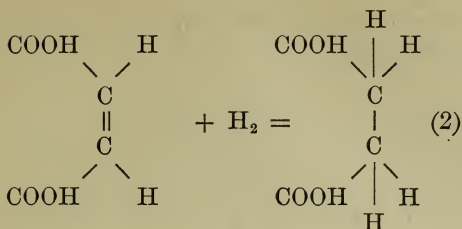


Upon treatment with potassium hydroxide the hydrobromic acid is withdrawn, and there is left the arrangement as assigned above to fumaric acid.

Both acids are converted into succinic acid by nascent hydrogen,

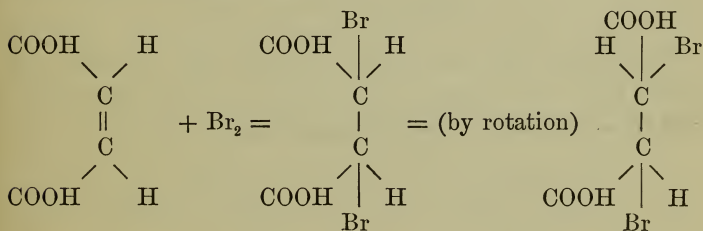


and

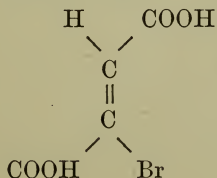


but by rotation of the lower carbon atom in (2) we should get the same arrangement as in (1), which is the most favorable configuration for stability for succinic acid. Similarly, it may be shown that both bodies would be converted into bromsuccinic acid by action of hydrobromic acid.

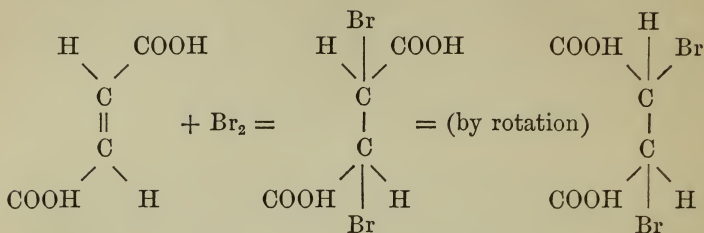
Again, if hydrobromic acid be removed from the bromine addition product of maleic acid, the result is bromofumaric acid, and if fumaric acid be subjected to similar treatment, the result is bromomaleic acid. These facts are represented by the following equations:—



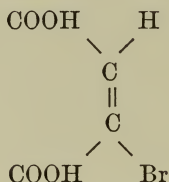
Then, by withdrawing the HBr, we obtain:—



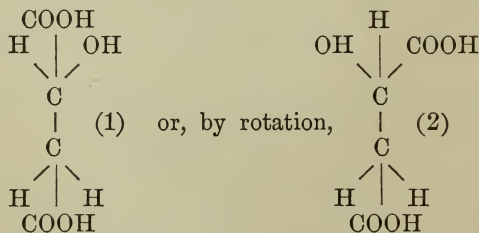
The other reaction may be similarly explained as shown by the following formulas, —



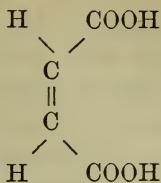
Then, by withdrawal of HBr =



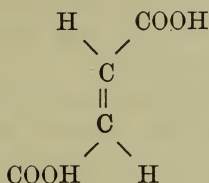
When malic acid is heated to 150°, both fumaric and maleic acids are formed, but the former is much more abundant than the latter. The formula for malic acid is: —



On subtracting H<sub>2</sub>O from (1) we get readily: —



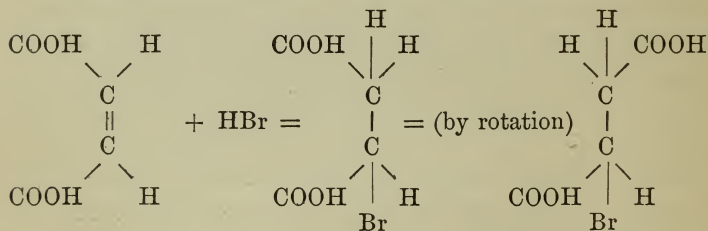
and from (2): —



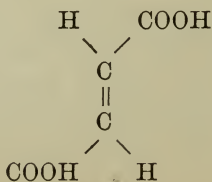
but since (2) is the configuration more favorable to stability, we should expect more molecules of the malic acid to possess this arrangement than the other, and therefore to have more fumaric than maleic acid produced. According to the theories enunciated, we should also expect that more of the less stable molecules of malic acid could exist at a higher temperature, and therefore that the decomposition yield of maleic acid would increase with rise in temperature. This has been found to be the case. Michael argues that no conclusions should be drawn from this reaction, because by further action of heat and water some of the maleic acid first formed must be converted into fumaric acid. To obviate this source of error, he did a similar experiment *in vacuo* at a temperature at which the maleic acid and water would be volatilized, and thus, as far as possible, removed from further action. Done in this way he found that at 180°–190°, he obtained from malic acid, to every 100 parts of fumaric acid, 27 parts of maleic acid, and at 200°–205°, 52 parts of maleic acid to every 100 of fumaric acid. Under the conditions under which

Wislicenus did his experiments he found at  $180^{\circ}$ – $190^{\circ}$ , 9–10 parts of maleic acid to 100 of fumaric, and at  $200^{\circ}$ – $205^{\circ}$  about 12 parts of maleic to 100 of fumaric. This shows that the relative proportions which can be obtained depend largely on the conditions under which the experiment is performed, but the general results are similar in the two cases; the amount of fumaric acid formed seems to be greater than that of the maleic, and the proportion of the maleic increases with the temperature.

Although many of the reactions of these acids are in complete accordance with the theories given and are readily explained by them, there are others, besides the one just mentioned, upon which some doubt has been cast, which cannot be so easily explained by these theories. One of these is the change of maleic into fumaric by the action of strong acids, especially HBr. Wislicenus attempts to vindicate his theory by supposing that bromsuccinic acid is formed as an intermediate product according to the following formulas: —



Then the HBr splits off again, leaving —





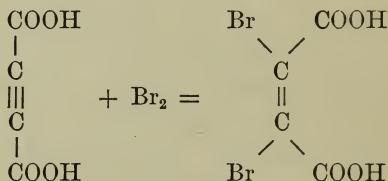
The objection urged against this explanation is that the bromsuccinic acid is stable and does not yield fumaric acid in presence of fuming hydrobromic acid. This objection is a strong one, but does not seem to be absolutely insuperable. It is conceivable that reactions may be possible in a molecule just formed in a changing system, which would not be possible in a mass of these molecules, after their stability had become fixed. However, Skraup<sup>1</sup> has made some investigation of this change, and also concludes from his experiments that Wislicenus's explanation is insufficient. He finds that the change from maleic to fumaric acid takes place through the influence of acid or water, and is also possible through other chemical processes. Only those acids which act chemically on maleic acid produce the change easily, though acids whose constituents cannot be added to the maleic acid, as nitric and sulphuric acids, *can* also produce this transformation. It might be urged that by the addition of water malic acid is formed as an intermediate product; but the fact that malic acid itself is not changed to fumaric under the conditions of these experiments makes this explanation improbable.

The explanation of the change which is adopted by Skraup, and also by Bischoff, is that small quantities of an addition product are formed, that this is not an *intermediate* product, but that by its catalytic action the transformation of maleic to fumaric acid takes place. As Bischoff expresses it, the addition is the *causal*, and the transformation the catalytically impelled process. As a general explanation of this and all catalytic action, Skraup states that in many chemical processes oscillations result, which may produce in other chemically disinterested molecules other oscillations, which, either by themselves or supported by other momenta such as

<sup>1</sup> Monatshefte f. Chemie, 12, 107.

heat motions, may effect a total change in the structure of the system.

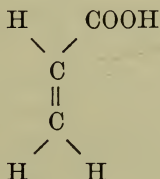
Another reaction which is more difficult to dispose of than the preceding in that it seems to really contradict a portion of the generally accepted theories, is that which takes place when bromine is added to acetylenedicarboxylic acid. According to Wislicenus, this reaction should give dibrommaleic acid:—



Bandrowski obtained as the result of this reaction principally dibromfumaric acid. Michael has repeated the experiments and finds both acids, about 30% being dibrommaleic, and most of the remaining 70% being dibromfumaric. Wislicenus reports as the result of his own experiments that dibrommaleic acid is the first product of the reaction, but that hydrobromic acid is formed at the same time, and if great care is not taken, a secondary reaction will take place and dibromfumaric acid be formed by the action of hydrobromic acid upon the dibrommaleic acid. He gives great prominence to the part played by HBr in this reaction. Meanwhile Michael states that he has left brommaleic acid mixed with hydrobromic acid under the same conditions as those in which the reaction with the acetylenedicarbonic acid took place, and did not find that bromfumaric acid was formed. Finally, having proved to his own satisfaction that both acids are normal addition products *in the presence of water*, he repeated experiments using an ether of the acetylenedicarbonic acid,

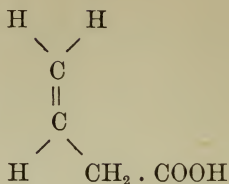
and bromine dissolved in carbon tetrachloride, to prevent the formation of hydrobromic acid, and obtained the same results. For an outsider who does not see these experiments performed, it is difficult to decide whose results to accept as trustworthy, but it is safe at least to say this, that we have here a reaction which has not been satisfactorily explained in terms of the theories given, and which casts some doubt upon the hypothesis suggested by Wislicenus; namely, that in changing from one form of linkage to another, the atoms keep their original relative positions.

The isomerism in the acrylic acid series <sup>1</sup> has also been the cause of much study and discussion. The first member of the series, acrylic acid, has the formula,



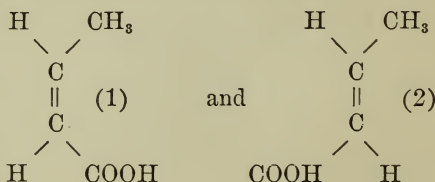
which shows no possibilities of isomerism. In accordance with this, only one acrylic acid has ever been obtained. For the second member of the series,  $\text{C}_3\text{H}_5(\text{COOH})$ , several different arrangements are possible. From a common method of preparation of the  $\alpha$  or solid crotonic acid, by treatment of allyl cyanide with potassium hydroxide, it was naturally given the formula: —

<sup>1</sup> Ber. 20, 1008, 1010; Ann. Chem. Pharm. 248, 281; Journ. prak-Chem. (2) 35, 257; Journ. prak-Chem. (2) 38, 6; Journ. prak-Chem. (2) 36, 174; Journ. prak-Chem. (2) 38, 1; Michael's Untersuchungen ueber Alloisomerie.



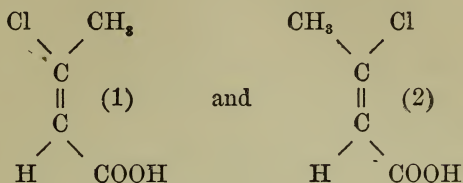
but Kekulé showed that its behavior toward fused alkalis was not in accordance with this formula, and that it should be written  $\text{CH}_3\text{CH} = \text{CH} \cdot \text{COOH}$ . In 1871 Geuther discovered liquid or iso-crotonic acid, and in some works on Organic Chemistry this is still given the formula once ascribed to the solid acid; namely,  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{COOH}$ , but it gives acetic acid with alkalis exactly as the  $\alpha$  acid does, and therefore the same reasons would hold good for giving it also the formula  $\text{CH}_3\text{CH} = \text{CH} \cdot \text{COOH}$ . More recently a true vinyl-acetic acid having the above formula has been prepared, and shown to be different from either of the crotonic acids.

We are left then with the two crotonic acids having the same structural formula. Assuming that they are geometrical isomers, they may be represented as follows:—

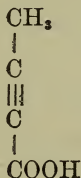


The question then arises, Is there any way of deciding which of these formulas should be ascribed to the solid and which to the liquid acid? Wislicenus answers this question in the affirmative, and draws his answer from the reactions

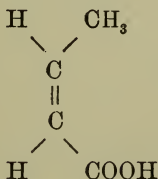
of the two  $\beta$ -chlorcrotonic acids with potassium hydroxide. The formulas for these two acids must be:—



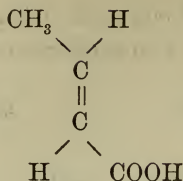
Both of them give with potassium hydroxide tetrolic acid:—



but (1) might naturally be expected to do this most easily. By experiment, the  $\beta$ -chlor-iso-crotonic acid is found to give off its hydrochloric acid much less easily than the  $\beta$ -chlor-crotonic acid, therefore formula (1) is given by Wislicenus to the normal acid, and (2) to the iso-acid. Correspondingly,



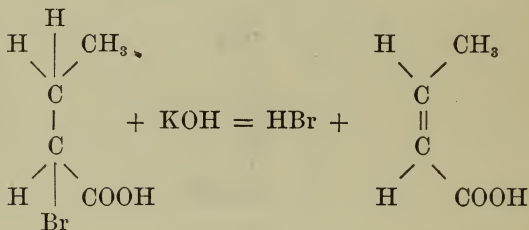
should represent the normal or solid crotonic acid, and



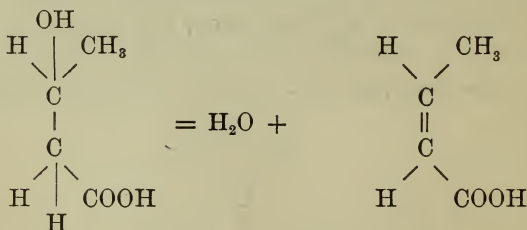
the iso or liquid acid.

Other methods of preparation of crotonic acid, showing its constitution, are the following:—

1.  $\alpha$ -brombutyric acid + KOH



2. Distillation of  $\beta$ -oxybutyric acid,

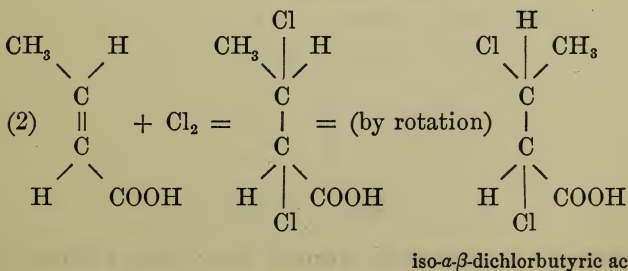
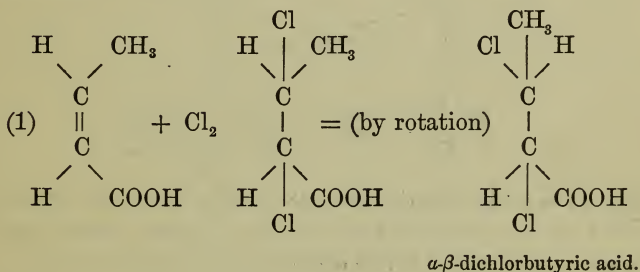


It may be interesting in this connection to note that the reaction between allyl cyanide and potassium hydroxide has been explained by the assumption that  $\beta$ -oxybutyric acid is first formed, and then that a further reaction takes place as just given. The principal fact in favor of this assumption is that

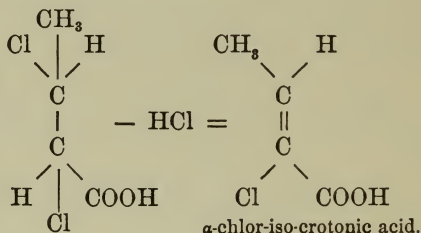


allyl cyanide is known under the influence of hydrochloric acid to undergo a somewhat analogous change, forming  $\beta$ -chlorobutyric acid, and then by the splitting off of hydrochloric acid to give crotonic acid.

In studying the reactions of the crotonic acids and comparing them with the results to be expected from the theories under consideration, we are met with the difficulty that different investigators report different results for the same experiment. Wislicenus, for example, reports that on addition of chlorine to solid crotonic acid, he obtains  $\alpha$ - $\beta$ -dichlorobutyric acid, and upon adding chlorine to the liquid crotonic acid, he obtains iso- $\alpha$ - $\beta$ -dichlorobutyric acid. These results agree perfectly with our theories, as is shown by the following equations:—

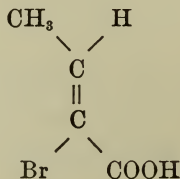


Michael, however, states that working with the purest possible acids, he obtained from reaction (1) a mixture of both  $\alpha$ - $\beta$ -dichlor acids, whereas in reaction (2) he obtains almost entirely the  $\alpha$ - $\beta$ -dichlorbutyric acid instead of the iso acid. There are a number of other reactions in which Michael obtains mixture of the normal and iso compounds where theory demands that only one should be formed, and in some cases he obtains the normal where the iso compound might be expected, and *vice versa*. As further illustration of this discordance in views, we may notice the reaction between  $\alpha$ - $\beta$ -dichlorbutyric acid and KOH. According to theory, the reaction should take place thus:—



and Wislicenus reports this to be the essential product as found by his experiments, whereas Michael states that he obtains a mixture of this with the  $\alpha$ -chlor-crotonic acid.

Again, Michael states that the addition of sodium amalgam to  $\alpha$ -brom-iso-crotonic acid:



gives solid crotonic acid, whereas theory would demand that it should be the corresponding iso acid.

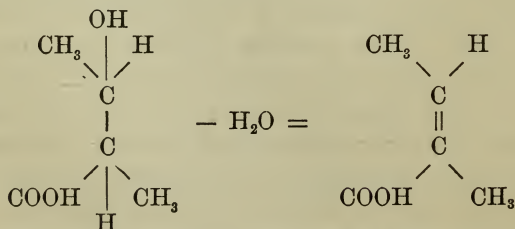
It is evident, then, that the crotonic acids have not yet met with the full and complete investigation which would be necessary in order that their reactions might properly be made use of either for the defence or overthrow of any theory. Wislicenus himself, in his recent Inaugural Dissertation, concludes that the liquid acid commonly called iso-crotonic is really a mixture of the two geometrically isomeric modifications, which is formed in all efforts to isolate the unknown, true iso-crotonic acid, on account of the great instability of the latter. This may prove to be the cause of the varied results obtained in working with the crotonic acids. At all events, the difficulty of preparing perfectly pure organic compounds, and of separating and recognizing closely related and similar products of a reaction, as also the ready change of a compound into its geometrical isomer, may be brought forward as adequate reasons for the contradictory statements in regard to the reactions of these acids. The difference in conditions under which the experiments are done must also have an effect upon the results. It is known that the liquid is converted into the solid crotonic acid at  $170^{\circ}$  to  $180^{\circ}$ , and that the influence of light is very noticeable in these reactions, and it may be that these two acids are converted into one another during the course of experiments by influences of whose effects we are not at present aware. This much is certain, that further experimental work is necessary before the complete bearing of these reactions on Wislicenus's hypothesis can be traced. The close relations between the two crotonic acids, the ready transformation of one into the other, and their similarity of reactions would seem to indicate that they are really geometrical isomers; that is, bodies whose isomerism can best be explained by van't Hoff's theories in regard to the relative positions of the atoms in space. The

only question which is brought into doubt by the conflicting reactions is in regard to Wislicenus's supposition that, in the formation of addition compounds, the atoms keep as nearly as possible their original positions.

The third member of the acrylic acid series,  $C_5H_8O_2$ , has two well-known representatives, — angelic and tiglic acids.<sup>1</sup> Angelic acid has been known since 1842; tiglic acid was first prepared in 1865 by Frankland and Duppa, who proved that it was isomeric with angelic acid. Since that time the isomerism of the two acids has been a common subject for investigation. Whether these two bodies are really geometrical isomers, or possess different structural formulas, still remains an open question, but their reactions seem to be better explained by the former assumption than by any structural formulas which have yet been assigned them.

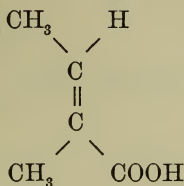
The fact that tiglic acid is made by heating angelic, that both, with potassium hydroxide, yield acetic and propionic acids, that they yield the same oxidation products with potassium permanganate, and the same reduction products with hydriodic acid, with many other similarities in chemical reactions, would indicate the closest similarity in their structural formulas.

The structure of tiglic acid is well shown by its preparation from  $\alpha$ -methyl- $\beta$ -oxybutyric acid:—

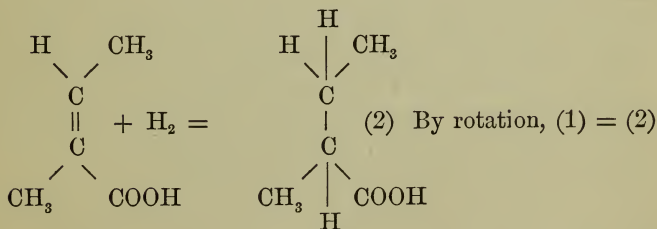
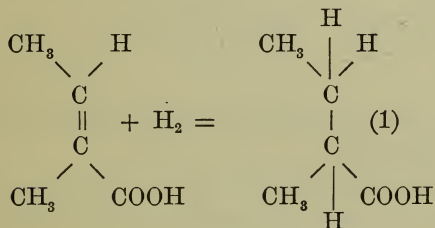


<sup>1</sup> Ann. Chem. Pharm. 250, 224; Guide to Lit. of Angelic and Tiglic Acids, by Henry P. Talbot, Ph. D.; Michael's Untersuchungen ueber Alloisomerie.

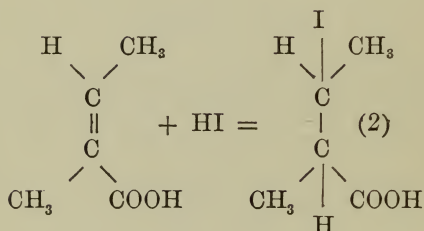
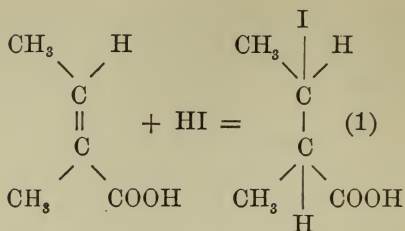
Assuming that these bodies are geometrical isomers, the above is the formula generally assigned to tiglic acid, and the following to angelic:—



Both acids are found to yield methylethylacetic acid upon reduction. This is readily seen to be in accordance with the formulas given:—

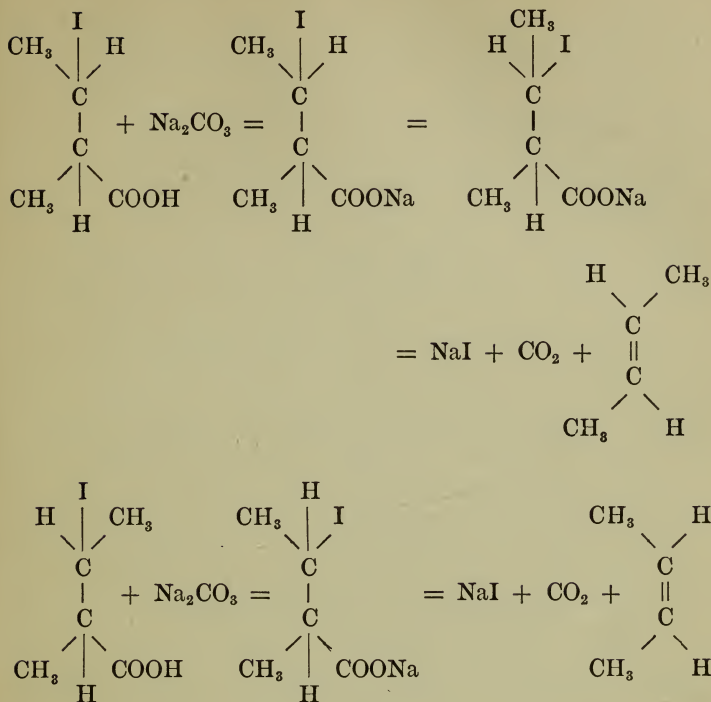


With hydriodic acid two different addition compounds are formed, differing slightly in physical properties, and similar results are obtained with hydrobromic acid:—



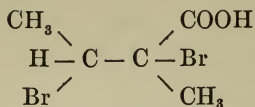
(1) and (2) are seen to be geometrical isomers, of which slight difference might be expected.

These two iodine acids treated with sodium carbonate each yield pseudobutylene, and, though there has been some difference of opinion as to whether it is one and the same pseudobutylene, or whether there are two geometrically isomeric bodies, Wislicenus describes minutely very careful experiments by which he and his pupils seem to have completely proved the latter. This is strictly in accordance with his theory as shown by the following equations:—

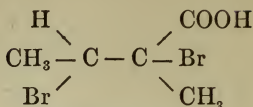


By the addition of bromine to angelic and tiglic acids, Wislicenus has succeeded in obtaining two different dibromides, differing slightly in melting-point, crystalline form, and behavior to certain reagents. In order to obtain this result, however, certain precautions have to be carefully observed; the process must be carried on at a low temperature, with little light, and care that the substance to be added shall be in large excess. To the two dibromides, Wislicenus gives the following formula:—



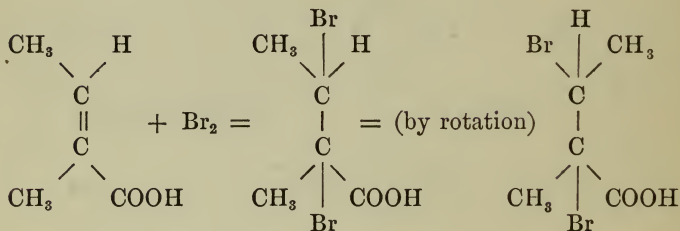
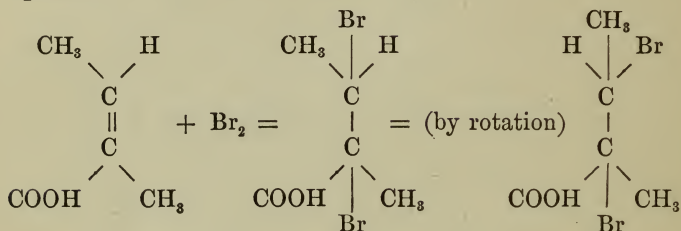


Angelic dibromide.



Tiglic dibromide.

The formation of these bodies is explained by the following equations:—



It should be mentioned, however, that Wislicenus's work with these acids has been warmly criticised by Fittig, who finds, for example, only one pseudobutylene resulting from the reactions in which Wislicenus obtains two geometrical isomers. In several other cases also he gets different results from Wislicenus, and results which are not as well in harmony with the theories advanced, so that a study of the reactions of angelic and tiglic acids leaves us in about the position in which we were after the study of the crotonic acids; namely, with the feeling that more work can very

profitably be done upon these bodies before we are in a position to decide whether their reactions are in entire accordance with Wislicenus's theories or not.

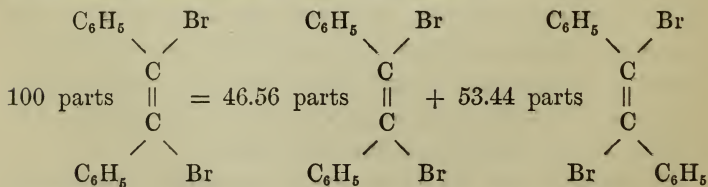
The facts seem to remain that in these and many other bodies, containing two doubly linked carbon atoms, we have cases of isomerism which cannot be explained by the use of structural formulas. Many of their reactions are in complete accordance with van't Hoff's and Wislicenus's views, so that this isomerism seems to be better explained by the use of their theories than by any other yet advanced. In some cases, the reactions seem to be in opposition to the theory that, in forming addition products, the atoms retain as nearly as possible their original positions. It may be that these reactions have not been sufficiently studied to make sure of their correctness. Granting that the adverse results as obtained *are* correct, we must remember that a body is always readily changed to its geometrical isomer, so that, under the conditions of the experiment, it may be possible that the change takes place before the addition, resulting in a product in which the atoms have shifted their position.

Wislicenus himself, in his recent Inaugural Dissertation, acknowledges that there are cases in which the abnormal addition product is formed in larger quantities than the normal, and that the yield sometimes consists almost entirely of the abnormal product. He finds that the amount of the abnormal addition product increases with the temperature, intensity of light, and length of duration of process, but in the pamphlet under consideration, limits himself to the discussion of the changes produced by heat.

He assumes that all atoms are in a state of oscillation around a middle point, and that this motion is increased by heat. As in many compounds this increased motion results

in decomposition, so in bodies containing asymmetric carbon or two doubly linked atoms it may result simply in a change of configuration. For example, many cases are known in which an active body becomes inactive under the influence of heat, because when the body has reached the mean temperature at which the change to the geometrical isomer is possible, one half the molecules are above that temperature and consequently an equal number of the right and left configurations are produced.

Wislicenus has determined the percentage amount of change from maleic to fumaric acid under different conditions. The quantitative change varies from 25.76% to 79.69%, the amount of fumaric acid increasing with the length of time that it is kept at a fixed temperature and also with the temperature, but a greater duration of time had more effect on the amount of change than increased temperature. With other compounds, particularly the tolane dichlorides and dibromides, he observed a tendency for the two geometrical isomers to reach the same final state of equilibrium at a high temperature, whichever isomer was taken as the starting-point. If the plane-symmetrical tolane dibromide, for example, be heated, the final result is that 46.56% of the original configuration is left unaltered, and 53.44% is changed to the centre-symmetrical body; that is, —



If, however, the centre-symmetrical body alone be heated, the final result contains 48.05% of the plane-symmetrical

isomer and 51.95% of the original centre-symmetrical body, a result which approximates the one given above.

These experiments suffice to show the easy transformation of a body into its geometrical isomer, the influence of the temperature upon the results which may be expected in any particular reaction, and some of the difficulties in the way of drawing definite conclusions as to the configurations of doubly linked compounds from a study of their chemical reactions.

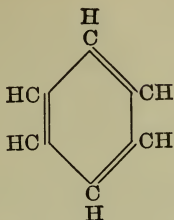
### III.

#### THE BENZENE SERIES.

THE preceding chapters have been devoted entirely to the study of open chains. Quite recently von Baeyer has attempted the stereo-chemical investigation of closed rings, the ultimate end of which must, of course, be to throw more light upon the constitution of benzene and its derivatives. This opens up afresh the whole interesting subject of the constitution of benzene, and it may not be out of place here to take a brief review of the work already done in that direction.

There are certain facts which must be represented in any satisfactory formula for benzene,—namely, the equality of all of the carbon atoms and, therefore, the impossibility of more than one mono-substitution compound; the capability of formation of three di-substitution products; the possibility of forming hexa-addition products and yet the fact that such compounds are formed with difficulty and show a tendency to go back to the simpler forms; the stability of benzene, which suggests a symmetrical formula; and the possibility of its formation from acetylene. These are only a few of the simpler facts which must be represented in a formula for benzene, and yet it is sufficiently difficult to find any formula which will perfectly satisfy these conditions.

In 1865 Kekulé<sup>1</sup> introduced the formula for benzene which has been in most common use,



and which is in fair accordance with most of the facts mentioned above. The symmetry of the molecule, the equality of the six carbon atoms, and the possibility of formation of a hexa-addition product are perfectly represented, and the possibility of its formation by the condensation of three molecules of acetylene is in better accord with this formula than with almost any other which has ever been suggested. The objections raised against it are principally that it admits of four di-substitution compounds instead of three, and that it does not explain the unwillingness of benzene to form addition compounds. On the contrary, since there are three ethylenic bonds, we should expect an eagerness to form addition compounds, and a tendency for the molecule to split at the points of double linkage. It was at one time suggested by von Baeyer<sup>2</sup> in regard to this, that the three double bonds in a closed ring might have a somewhat different action from what they would in an open chain, the tendency to form addition compounds being counterbalanced by the gravitation of the atoms toward the centre of the molecule, but this idea

<sup>1</sup> Bull. Soc. Chem. (2) 3.98; Ann. Chem. Pharm. 137, 129.

<sup>2</sup> Ber. 23, 1272.

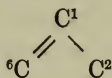


would perhaps be better expressed by Armstrong's<sup>1</sup> modification of Kekulé's which he calls the centric formula:—



In this, the energy is represented as directed toward the centre of the molecule instead of holding together any two particular atoms.

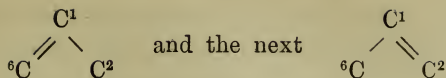
In regard to the objections urged against Kekulé's formula with reference to the di-substitution products, while it is true that 1 : 2 and 1 : 6 —



are not strictly identical, it seems natural to expect that the difference between these two ortho compounds would be less than between the ortho and meta, or ortho and para, and it is quite conceivable that the differences might be so slight as to escape observation altogether. Kekulé himself has endeavored to reconcile his formula with the existence of only three di-substitution products, by the assumption that the bonds indicate vibrations, and that two atoms joined by single bonds approach one another twice as often in a given time as two atoms with double bonds, that  $C_1$  approaches  $C_2$  twice, then  $C_6$  once, but then reverses, and approaches  $C_6$  twice and  $C_1$  once. This makes a constantly shifting formula, being one moment

<sup>1</sup> J. Chem. Soc. 51, 264.





The problem of the constitution of benzene has also been attacked from the physical side. Julius Thomsen, whose work will be reviewed more in detail later, decided at one time from his thermo-chemical investigations, that the six carbon atoms of benzene must be bound together by nine single bonds instead of six single and three double, and therefore rejected Kekulé's formula. On the other hand Brühl,<sup>1</sup> working in 1887, gave support to Kekulé, deciding from optical considerations that double bonds must be present.

Claus's diagonal formula, introduced in 1867, differs from the centric formula given above only that in this the diagonally opposite carbon atoms are represented as bound together.



This claims the advantage over Kekulé's, in that it shows the possibility of only three di-substitution products, and it does away with the ethylenic bonds. It has, however, certain disadvantages. It does not seem in as complete accordance with the formation of benzene from acetylene as Kekulé's formula does, and it leaves no explanation for the formula for naphthalin. Moreover, using this formula, we have to admit the possibility of the formation of addition products by the breaking of *single* bonds.

<sup>1</sup> Ber. 21, 2288; 20, 562.

These same objections apply to the much-discussed prism formula of Ladenburg, introduced in 1876, which represents the six carbon atoms as lying in the solid angles of a right-angled prism on a triangular base. Another criticism which has been brought against this is that it is an unsymmetrical figure, but if the upper triangle be rotated through  $180^\circ$  and then projected on a horizontal plane, a star-like symmetrical figure is produced. This shows as well as the other formulas the possibility of only one mono-substitution product and three di-substitution compounds. This formula has met with some very strong support, and has the prestige of being the first attempt at a stereo-arrangement for the benzene molecule.

Only one other formula need be mentioned here, the one introduced by Dewar in 1867,



but this seems to have no essential advantages over Kekulé's. The formation of benzene from acetylene is well represented, and it is in accordance with Graebe's naphthalin formula; but here again the *hexa*-addition products cannot be formed without losing the single bonds, and, moreover, there are apparently two different kinds of carbon atoms, and therefore the possibility of two mono-substitution compounds is represented.

In 1880, Julius Thomsen<sup>1</sup> undertook to decide the number of single, double, and triple linkings in organic compounds, by thermo-chemical investigations. He deduced a formula

<sup>1</sup> Ber. 13, 1388, 1808, 2166.

in which the heat of formation of a hydro-carbon is shown to be a function of the number of double, single, and triple linkings. The results as calculated from this formula agree fairly well with the observed heats of formation in the case of the paraffins, and also in the case of the olefines if we assume the formulas, as generally adopted, with one double linking in an open chain rather than a closed ring with all single linkings. Applying his formula to benzene, he found that the calculated value agreed most nearly with the observed value if he assumed nine single linkings instead of six single and three double. He, therefore, at that time accepted Claus's or Ladenburg's formula rather than Kekulé's and some later experiments,<sup>1</sup> comparing the heat of combustion of benzene with that of dipropargyl and of acetylene seemed to be in accordance with this idea.

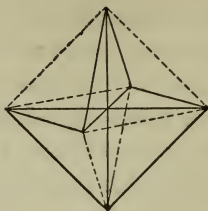
Of the two formulas, he preferred Ladenburg's to Claus's as satisfying the need for an arrangement *in space* of the six carbon atoms, but in 1886 he writes that on account of the lack of symmetry of the prism formula and its want of agreement with certain chemical considerations he does not find it entirely satisfactory, and suggested instead an octahedral symbol,<sup>2</sup> since a perfectly symmetrical arrangement in space of six carbon atoms would lead to the regular octahedron.<sup>3</sup> According to this theory, then, the six carbon atoms are regularly distributed in a spherical surface, and correspond to the solid angles of a regular octahedron. The three axes of the octahedron hold together three pairs of carbon atoms. Each atom is joined to two neighboring atoms through an edge, and to a third through an axis of the octahedron. (See figure,

<sup>1</sup> Ber. 15, 328.

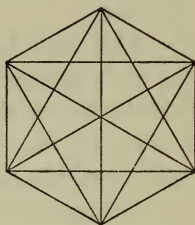
<sup>2</sup> Ber. 19, 2944.

<sup>3</sup> Such a symbol had been previously suggested by R. Meyer in 1882 (Ber. 15, 1823).

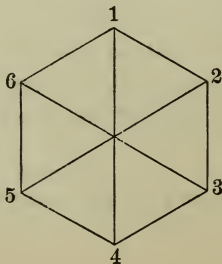
in which the heavy lines indicate the linkings between the atoms):—



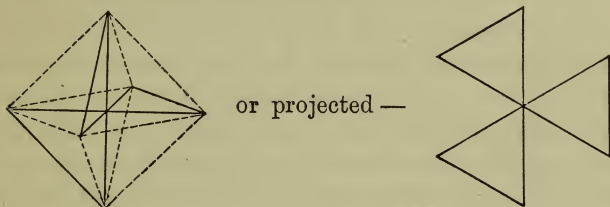
This symbol fulfils the necessary condition of having all the carbon atoms equal, and shows the possibility of having three and only three di-substitution products. This is shown more plainly by the use of the *projection* of the octahedron, which is a regular hexagon:—



If now, of the twelve edges of the octahedron, those are taken away which are not used in the constitution of benzene, the following figure results:—



This figure is exactly like Claus's diagonal formula for benzene, but with a very different idea behind it. This now represents the projection of a solid figure, and the diagonal bonds are the axes of the octahedron — 1 : 2, and 1 : 4 differ in that one is a peripheral, the other an axial combination. According to Thomsen, the addition products result through loosing of the peripheral bonds, and three such bonds can be loosed without the octahedral form being destroyed. (See figures.)



According to this, the axial or diagonal bonds cannot be loosed, since they are the essential basis of the octahedral form, whereas in Claus's formula, the diagonal bonds represent energy in excess of that necessary to hold the molecule together, which can be used in the formation of addition products.

Thomsen himself, however, soon brought one objection against his own formula. It was that if this formula be correct, benzene might be expected to crystallize in the octahedral instead of the rhombic system. And more recently<sup>1</sup> he has altogether discarded this formula together with his former views that benzene must contain nine single bonds. He finds that in the case of trimethylene the calculated heat of combustion agrees with that observed, only on the supposition that trimethylene contains three half-double bonds.

<sup>1</sup> Zeit. ph. Chem. 7, 55.



He concludes, therefore, that a double bond consists of two single bonds which partially neutralize each other, and from further experiments, he decides that in benzene there must be more than one kind of linkage and that his formula for heats of formation can be used only by ascribing to benzene three double bonds. All objections to Kekulé's formula are therefore withdrawn by Thomsen just at present.

Kekulé's, Claus's, Ladenburg's, Armstrong's, Dewar's, and Thomsen's are then the principal formulas which have been proposed for benzene; and though none of them are without merit as symbols to represent the properties of benzene, no one of them is so perfect and so plainly superior to the rest as to be accepted without cavil by all. It is to be noticed that all of these theories are entirely independent of the nature, shape, etc., of the carbon atom, and are concerned only with the way in which the carbon atoms are united.

The most recent work in connection with benzene has been done by von Baeyer, who, beginning in 1885 with a study of the polyacetylene derivatives, considered next the general subject of ring formations, and finally turned his attention almost entirely toward the aromatic series, the most important and best known of the closed ring compounds. Von Baeyer has prepared a number of new acetylene and di-acetylene derivatives, his object being to build up longer carbon chains and study their properties.

Among such compounds prepared, and first described in a paper published in March, 1885, is di-acetylene-dicarboxylic-acid-ether  $C_2H_5-CO_2-C \equiv C-C \equiv C-CO_2-C_2H_5$ . This, he says, explodes violently at about  $177^\circ$  with separation of a very voluminous coal, and adds that this is, to the best of his knowledge, the first example of a compound being explosive which is made up only of carbon, hydrogen, and oxygen. It

is to explain the explosibility of the acetylene derivatives, and the greater explosibility with increase of number of carbon atoms in the chain, that he adopts what is frequently referred to as von Baeyer's *strain* theory.<sup>1</sup> He argues that, to account for the explosibility of such compounds, much heat must be set free in the change to ordinary coal of acetylenic carbon, and accounts for this by the supposition that in the acetylenic condition there is some strain in the molecule, which in the change to coal is set free in the form of heat.

Von Baeyer's articles of belief in regard to the carbon atom are as follows: that it has four equal valencies which are regularly distributed in space and correspond to the angles of a regular tetrahedron inscribed in a sphere; that the carbon atoms can combine with one another either with one, two, or three bonds, forming either open or ring-like closed chains; and that the four valencies of the carbon atoms work in the directions which bind the middle point of the sphere with the tetrahedral angles, and which make with one another angles of  $109^{\circ} 28'$ . He further adds: *the direction of the attraction can undergo a deviation which has as its consequence a strain increasing with the amount of the deviation.*

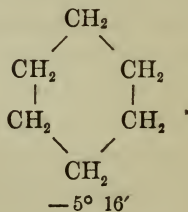
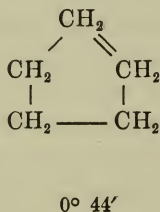
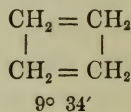
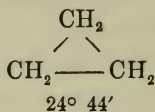
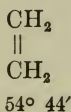
To illustrate this last point he refers to the common models in which the carbon atom is represented as a ball from which wires project, making with each other angles of  $109^{\circ} 28'$ . If such models be joined together they will form either a zigzag line, or a closed ring of five atoms. If we wish to make with them a ring of more or less than five atoms, the wires must be bent from their original positions, inducing a kind of *strain*, and something entirely analogous to this von Baeyer conceives to take place in the carbon atoms themselves.

As an illustration of this idea when applied to carbon com-

<sup>1</sup> Ber. 18, 2277; 23, 1272.



pounds he considers the rings built up of several methylene groups. Of these the simplest is ethylene. To produce this from ethane, two of the bonds must be bent until they are parallel. Supposing both bonds bent equally, each must be turned through an angle  $\frac{1}{2} (109^\circ 28') = 54^\circ 44'$ . To form trimethylene, which may be pictured as an equilateral triangle, the angle must become  $60^\circ$ , and each bond must be turned through  $\frac{1}{2} (109^\circ 28' - 60^\circ)$ . In tetramethylene the deviation will be represented by  $\frac{1}{2} (109^\circ 28' - 90^\circ)$ . Pentamethylene may be represented as a regular pentagon whose angle is  $108^\circ$ ; therefore the amount of deviation necessary is only  $\frac{1}{2} (109^\circ 28' - 108^\circ) = 44'$ . With hexamethylene, the derivation becomes  $\frac{1}{2} (109^\circ 28' - 120^\circ)$ . These facts are shown at a glance by the accompanying figures, the angle of deviation from the normal direction of the valence being given in each case: —



From these formulas, it is seen that the greatest "strain" comes in the ethylene, and this agrees well with fact in that this is the one which is most ready to form addition compounds, being readily attacked by hydrobromic acid, bromine,

and even iodine. Trimethylene is attacked only by bromine, and tetra and hexamethylene not at all, or only with great difficulty by any of these reagents.

It would follow from these ideas that triply linked compounds should be more unstable than doubly linked, since the larger the number of bonds bent from their normal position, the greater the strain would be; and this view meets with some support from Thomsen, who has found from calorimetric measurements that by the transformation of a double linkage into a triple, there is an essential lessening of the stability of the system under consideration.

Adopting these views, we should expect five-atom carbon rings to be formed more readily and be more stable than the rings composed of six atoms, whereas the former are found only seldom and in complicated compounds. Von Baeyer remarks in this connection that the objection is not of great weight, because the six-atom ring is found principally in the benzenes which are poorer in hydrogen, and that under exactly similar circumstances, it is quite possible that pentamethylene would be formed a little more easily and be a little more stable than the hexamethylene. Victor Meyer<sup>1</sup> thinks that a possible explanation may be found in the greater symmetry of the six-atom ring, which is conducive to stability, and calls attention to the fact that the angle of deviation in hexamethylene, though larger than that in the case of pentamethylene, is still quite small.

To sum up briefly this portion of von Baeyer's work, he adopts van't Hoff's idea of the valencies of the carbon atoms working in the directions of the angles of a tetrahedron, assumes that these valencies can be bent from their normal position producing a strain, that the greater this strain the

<sup>1</sup> Ber. 23, 580.

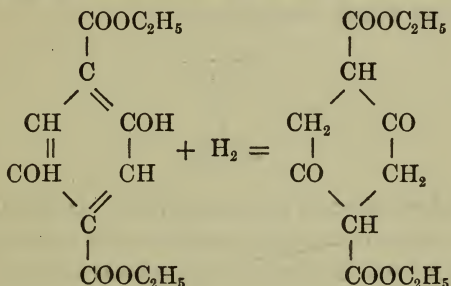
more unstable the body will be, that if the carbon atoms be arranged in a plane, five or six such atoms will form a closed ring with no or very slight deviation from the normal direction of the valencies, and that such bodies may, therefore, be expected to be stable. Since benzene and its derivatives are stable bodies containing rings of six carbon atoms, he concludes that in these bodies the centres of gravity of the carbon atoms lie in a plane instead of being distributed in space.

All of the later work upon the aromatic series is based upon this last conclusion, although von Baeyer's strain theory is open to some criticism. That theory adapts itself well to wooden models with wire valencies, but until we have a more definite idea of what the valencies of an atom really are, it is difficult to get any clear idea of what this "strain" may be. It will be noticed that the strain hypothesis originated in the explosibility of the acetylene derivatives; and Victor Meyer<sup>1</sup> calls attention to the fact that silver oxalate is very explosive, although the conditions considered necessary by von Baeyer in his investigations are altogether lacking. He also thinks the fact that acetylene is the only hydrocarbon formed by the electric spark from carbon in an atmosphere of hydrogens shows a stability of acetylene incompatible with the existence of the great strain which von Baeyer's views would demand.

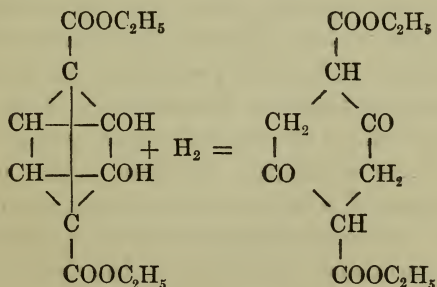
Whether von Baeyer's work be accepted in its entirety or not, it must certainly be acknowledged that it has proved very fruitful. Having arrived at the conclusion that the six carbon atoms must lie in a plane, he has done many experiments in the endeavor to reach some basis of decision between the plane formulas already mentioned.

<sup>1</sup> Ber. 23, 581.

A part of his earlier work in this direction<sup>1</sup> consisted in the proof that hexamethylene and hexahydrobenzole were really identical. This proof consisted in the transformation of dioxyterephthalic acid, by reduction, into succinylo-succinic acid, which is a hexamethylene derivative. Since the dioxyterephthalic acid is a para compound, the reaction, using Kekulé's formula, is represented by the following equation:



In this reaction there is evidently an addition of two hydrogen atoms and a change of position of two others, and two para positions are retained. Von Baeyer makes use of this reaction to prove the prism formula untenable. Using Ladenburg's formula, this same reaction must be represented as follows:—



<sup>1</sup> Annalen der Chem. 245, 103.

The reaction expressed in this way involves a change in position of the oxygen atom and seems somewhat complicated and improbable. Moreover, von Baeyer argues against the prism formula as follows: The prism consists of two triangles held together by three para edges. In order to get a hexamethylene from this, two of the triangular bonds and one of the para edges must be broken; for if we endeavor to break *two* para edges, we obtain, —



which would represent a ditrimethylene. In the above transformation, however, two para positions are retained; but this would demand the breaking of the corresponding para edges in order that the hydrogen atoms might be substituted in those places, which has just been shown to be impossible. He therefore concludes that only Kekulé's and Claus's formulas need be taken into consideration.

Ladenburg, however, does not submit quietly to being thus put out of the contest, but protests<sup>1</sup> that von Baeyer gives evidence against the prism formula and new evidence in favor of the hexagon without bringing any arguments against the former evidence in favor of the prism, and accordingly that both formulas are possible. He still holds to his opinion that the prism formula is the only one which can give a clear idea of the benzene *substitution* products, while agreeing that Kekulé's formula is better adapted to explain certain other reactions. He therefore concludes that the assumption which is in best accordance with facts is that the benzene nucleus

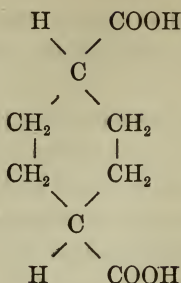
<sup>1</sup> Ber. 20 62.



can exist in two forms, — a more stable form corresponding to the prism, and a less stable form corresponding to the hexagonal formula.

Although the prism formula was rejected by von Baeyer, he also, some years later, came to the conclusion that the exact configuration of the nucleus might be different in different benzene derivatives. His work leading to this decision is so interesting and important that it seems well worth while to review it briefly, whatever may be considered the definite outcome of his studies. Having come to the conclusion that benzene consists of six CH groups, with the centres of gravity of the six carbon atoms lying in one plane, it was with the ultimate object of determining how these groups were joined together that von Baeyer undertook his work with the reduction of the phthalic acids. The comprehensive scope and the value of his work in this direction, leading as it did to some interesting illustrations of geometrical isomerism in the aromatic series, cannot be praised too highly even if it does not lead positively to a satisfactory formula for benzene.

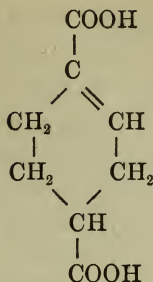
When terephthalic acid is acted upon by sodium amalgam, two hydrogen atoms are added in the cold, when heated four atoms are added, and with great difficulty six atoms of hydrogen can be added, forming respectively di-, tetra-, and hexahydroterephthalic acids. The last of these can better be prepared by the reduction of the hydrobromide of tetrahydroterephthalic acid, and has the constitution represented by the following symbol: —



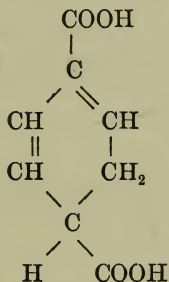
This substance exists in two geometrically isomeric forms and acts in all particulars like a saturated body. It is not attacked by potassium permanganate in the cold; when heated, bromine acts upon it and is substituted in the  $\alpha$  position. This last product is isomeric with the addition product formed by adding hydrobromic acid to the tetrahydroterephthalic acid. These two isomers differ in properties, but by addition of alcoholic potash to both, one and the same tetrahydroterephthalic acid results, and this is identical with the acid produced by direct reduction of terephthalic acid.

These reactions show that in the tetra-acid produced by the reduction of terephthalic acid, the double bond must be connected with the carbon attached to carboxyl, and von Baeyer has proved by three different reactions that this double bond must lie between two *adjacent* carbon atoms. Only one reaction in support of this idea need be given here. The di-addition product formed by adding bromine to tetrahydrophthalic acid has been converted into a product identical with tetrabromopyrocatechin. This would indicate that the extra bonds lay in the ortho position. Accordingly, the formula for tetrahydroterephthalic acid is written:—





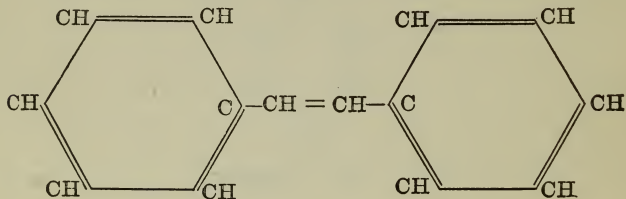
By somewhat similar methods he deduces the formula for the dihydroterephthalic acid formed by reduction to be: —



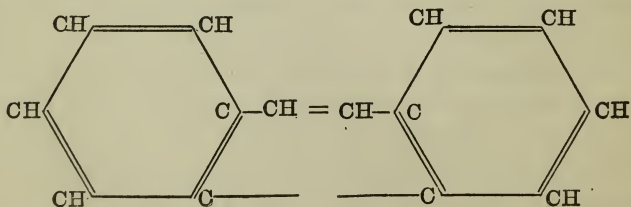
These formulas are in accordance with facts in that the di- and tetra-hydro acids act exactly like the acids of the unsaturated series with ethylenic bonds, taking up bromine instantly under the same conditions as the cinnamic acids.

The question now is, can we go back from these formulas to the formula for terephthalic acid, and thus to the formula for benzene. Adopting the formula for the di-addition product, that one which lies nearest to the terephthalic acid, the simplest supposition would be that Kekulé's formula was correct; but here we are met again by the old objection that terephthalic acid and benzene do not act like unsaturated

bodies, as might be expected if they had three ethylenic bonds. On the other hand, if the *diagonal* formula be adopted, we must suppose that the first addition is made by the breaking of a *single* linkage, and that straightway the other two diagonal bonds go over into ethylenic. These ideas would be as well, and perhaps better, represented by the centric formula, and von Baeyer was at first inclined to accept this, rejecting Kekulé's principally on the ground that the benzene derivatives are stable toward potassium permanganate; whereas double bonds, either in open or closed rings, he supposed to be instantly attacked by that reagent. In 1889, however, he reversed that decision,<sup>1</sup> since it had been shown in the mean time that under some circumstances a double bond in a ring formation could resist this action. Stilbene



is immediately oxidized by potassium permanganate in the cold, but the similarly constituted phenanthrene



is not attacked.

<sup>1</sup> Annalen der Chem. 251, 256.

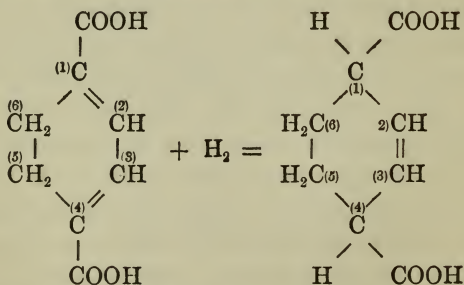
Since here is a body containing double bonds which is not affected by potassium permanganate, the fact that benzene resists that reagent is no proof that it has not double bonds. On the supposition that the three double bonds in the closed rings have a somewhat different nature from that in the open chain, the internal force of gravitation neutralizing the ordinary tendency to instability, he concludes that the reactions of terephthalic acid are explained equally well by Kekulé's and by the centric formula.

In an address made in 1890 at the festival in honor of the 25th anniversary of Kekulé's most important discoveries, von Baeyer<sup>1</sup> announces his conclusion that the valence in the benzene molecule itself can no more be expressed than that in a molecule of nitrogen; it is, like the nitrogen molecule, a stable whole, and its free bonds only make their appearance when the structure of the kernel is disturbed at some point. The aromatic series may be divided into groups differing somewhat as to the way in which the carbon atoms are held together. The *most stable* compounds are benzene and its immediate derivatives, the carboxylic acids, etc. These appear as the "Ideal" in which the CH groups are so firmly bound together that the valence of the carbon may be considered as three rather than four, the double bonds appearing only under certain circumstances. The *loosest* benzene compound is phloroglucin, in which there are undoubtedly three double bonds, which are only a little more stable than those in bodies of the fatty series. Bodies such as naphthalin and phenanthrene take a medium position, since they add halogens, but are stable against potassium permanganate. The two extreme limits of the benzene derivatives may then be expressed by Kekulé's and the centric formulas. Von Baeyer

<sup>1</sup> Ber. 23, 1272.

concluded at that time that the nature of the benzene ring in any derivative may correspond to a state lying midway between these two, and therefore that Kekulé's formula can well be retained for common use.

Von Baeyer's object in all his work was, as he has stated, not to prove or disprove any particular formula for benzene, but in so far as possible to arrive at the truth; therefore he is ready to change his views when new discoveries seem to make it necessary, and in 1892,<sup>1</sup> on the basis of newly discovered facts, he gives the preference to Claus's diagonal formula. In the paper in which he endeavors to prove that this formula is in better accordance with observed facts than any of the others, he starts out with the decision that no conclusions can be drawn as to the constitution of benzene from the reduction of a benzene derivative. This decision is forced upon him by observations which show a serious mutability of the double bonds, and an addition of hydrogen where it would least be expected. He finds, for example, that  $\Delta^{1,3}$  dihydroterephthalic acid gives by reduction  $\Delta^2$  tetrahydroterephthalic acid, according to the following equation: —

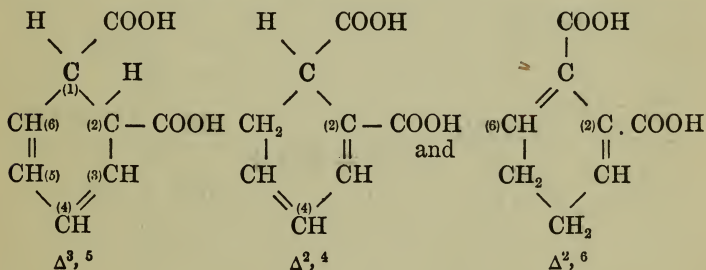


<sup>1</sup> Lieb. Ann. der Chem. 269, 145.

<sup>2</sup> The numerals indicate the carbon atoms which are connected by double bonds with the next carbon atom, going around the ring in the direction of the hands of a watch.

Other observations of a similar kind led him to conclude that the hydrogen atoms wandered sadly, and that one could not draw any inferences from the constitution of a reduction product as to the constitution of the original body. Accepting these observations as correct, we shall have to conclude that his work with the phthalic and terephthalic acids, although extremely valuable on account of the new isomers described, are not of importance in connection with the use to which he hoped to be able to put them; namely, to discover the constitution of benzene.

Von Baeyer, however, affirms that the reverse action, the building up of the benzene nucleus from a hydro derivative, *can* furnish a clew to the nature of benzene, and concludes that the facts from this standpoint are in favor of Claus's formula. Only a very brief outline of the observations which led him to this conclusion can be given here. He points out that the three following dihydrophtalic acids yield by oxidation benzoic acid and carbon dioxide:—



The  $\Delta^{3,5}$  acid undergoes this reaction with the greatest ease, even with very weak oxidizing agents. Von Baeyer's explanation is that the withdrawal of hydrogen sets the  $\alpha$  carbon into violent vibration, whereby the carboxyl is separated off, and the same explanation is applied to  $\Delta^{2,4}$ ; but in  $\Delta^{2,6}$ , the





In this same article, von Baeyer brings forward another argument against Kekulé's formula. This, he says, would demand two phthalic acids, — one in which the two carboxyl-bearing carbon atoms are joined together by double bonds, and another in which they are singly linked; but two different bodies have never been found. The one in which the carbons are connected by single bonds might be expected by taking away hydrogen from  $\Delta^{2,6}$  dihydrophthalic acid; but instead, as has been seen, benzoic acid is formed, while that acid which has a double bond between the  $\alpha$  carbon atoms produced phthalic acid.

The reactions described above are certainly indications in favor of Claus's formula; but without further evidence it would seem that they should not be accepted as *proof* of direct linkage between para atoms in all aromatic compounds, since other reactions have been observed which show, with perhaps equal force, the improbability of such linkage.<sup>1</sup> Brühl's study of the optical and physical properties of organic bodies has led him to the conclusion that benzene contains three ethylenic bonds, on the ground that the change in these properties in passing from benzene to dihydrobenzene is not sufficiently marked to warrant the supposition that there is a great difference in the molecular structure of these two bodies.<sup>2</sup>

A careful study of all the work done in connection with the constitution of benzene seems to leave us with no entirely satisfactory outlook, although a large amount of valuable material has been collected to aid in elucidating the problem, which, it may be hoped, will be solved at some not-far-distant date. Meanwhile, there seem to be many reasons, in the present state of our knowledge, for giving the preference to

<sup>1</sup> Am. Chem. Jour. 12, 463; 13, 422.

<sup>2</sup> J. pr. Chem. [2], 49, 201; Ber. 27, 1065.



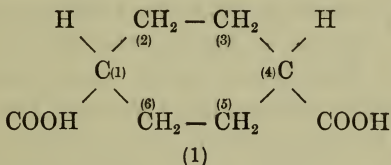
the centric formula, as expressing the reserve energy of the benzene molecule without giving too definite a location to that energy. If further experiments should give more conclusive evidence of direct linkage between para atoms, then it would be necessary to localize that energy and change from the centric to the diagonal formula. Kekulé's formula is open to the very serious objection of showing ethylenic bonds which in other compounds have a definite meaning which they do not possess in the benzene nucleus. Von Baeyer's suggestion that the active power of these double bonds may be partially lost in a closed ring, being neutralized by the attraction toward the centre of the atoms composing the ring, seems a practical abandonment of Kekulé's for the centric formula.

It will be readily seen that we are not in very good condition at present to make any suppositions in regard to the three-dimension configuration of the benzene molecule. All of the work thus far done has been based on the supposition that the centres of gravity of the carbon atoms composing the benzene ring lie in a plane. Von Baeyer says that the material is far too meagre at present for any conclusions to be drawn in regard to the actual arrangement in space of the benzene molecule, and others protest against a too hasty effort to apply three-dimension formulas to the aromatic series.

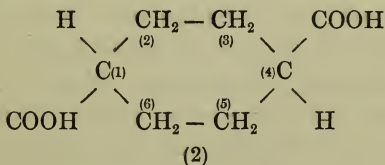
The first contribution to our knowledge of geometrical isomerism in the benzene series was made by van't Hoff in 1875, when he pointed out that in hydromellitic and isohydromellitic acids we have two bodies whose isomerism must rest on a difference of space configuration of their molecules.

Von Baeyer, in his study of the hydrogen derivatives of the phthalic acids, observed that there were two isomeric hexa-addition products. Each can be readily converted into the other; but they differ in solubility and other physical proper-

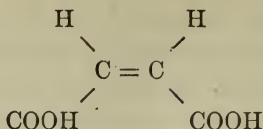
ties in a way entirely comparable to the geometrical isomerism noticed in olefine derivatives. Von Baeyer explains this on the assumption that the carbon atom has its valencies in the directions of the angles of a tetrahedron, and that in the benzene nucleus the six carbon atoms are found with their centres of gravity in a horizontal plane. In hexamethylene, then, the two hydrogen atoms attached to each carbon will lie in a plane perpendicular to the horizontal plane, and the twelve hydrogen atoms will be equally distributed in two planes, one above and the other below the plane containing the six carbon atoms. If now one hydrogen atom be removed from each of two carbon atoms in the para position to each other and be replaced by carboxyl, the result will be hexahydroterephthalic acid, and we may have two isomeric bodies according to whether both carboxyls are in the same or in different planes. As well as this can be shown on a plane surface, the two geometrical isomers would be represented as follows:—



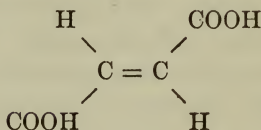
and



Of these (1) is called the *cis* acid, or the maleinoid, on account of its resemblance to maleic acid:—



and (2) the *trans*, or fumaroid, since the carboxyls are on opposite sides, as in fumaric acid:—

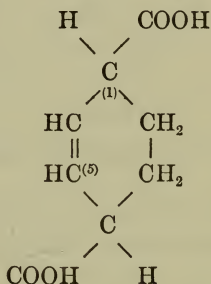
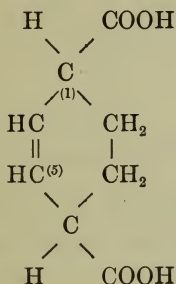


The general characteristics of these different acids correspond also to the differences in properties of maleic and fumaric acids. The *cis* acids are more easily soluble, have a lower melting-point, and are stronger acids than their *trans* isomers, thus resembling maleic acid; but the *trans* acids, like fumaric acid, are more stable, as is shown by the fact that they may be produced by the direct transformation of the *cis* acids; as, for example, by heating with hydrochloric acid.

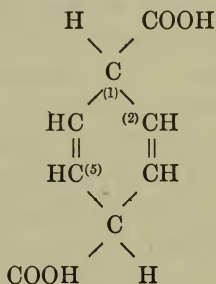
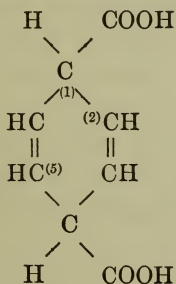
In the above formulas, the carbon atoms numbered (1) and (4) are asymmetric, because if (1) be moved from right to left around to (4) the carboxyl will be on the right of the carbon atom, whereas, if moved to the same position from left to right, the carboxyl will be on the left. Hence it follows that the two affinities of (1) are not bound in the same way, and that it is, therefore, asymmetric. This is called *relative asymmetry*, and it is characterized by the fact that the asymmetry of one of the two carbon atoms is compelled by that of the other, for if the carboxyl of (4) be replaced by hydrogen, the asymmetry of (4) and (1) vanishes simultaneously. This kind of asymmetry, however, is not a kind limited to the aromatic

series, but is simply a special case of the geometrical isomerism observed in the unsaturated bodies, for it will be recalled that if, in maleic and fumaric acids, one carboxyl be replaced by hydrogen, all possibility of isomerism is at once lost.

Similarly, isomerism has been observed in the tetra- and di-hydrophthalic acids, an isomerism explained by the following formulas: —



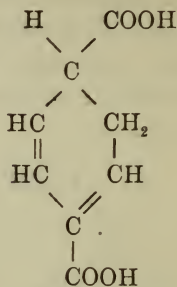
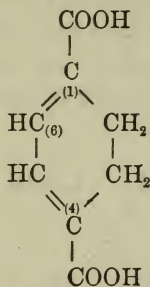
$\Delta^5$  *cis*tetrahydroterephthalic acid, and  $\Delta^5$  *trans*-tetrahydroterephthalic acid.



$\Delta^2, ^5$  *cis*dihydroterephthalic acid, and  $\Delta^2, ^5$  *trans*-dihydroterephthalic acid.

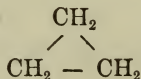
The number of possible isomeric forms of the hydro acids is quite large, since they are capable of *geometrical* isomerism, as shown above, and also any different arrangements of the double bonds gives a new isomeric form. For example, beside

the two dihydroterephthalic acids whose formulas are given above, we may have:—



$\Delta^{4,6}$  dihydroterephthalic acid, and  $\Delta^{3,5}$  dihydroterephthalic acid.

It thus becomes possible, theoretically, to have fifteen hydrophthalic acids, and of these<sup>1</sup> eleven are known and their constitution quite well determined. It has been von Baeyer's great work to prepare, purify, and determine the constitution and properties of these different isomeric bodies, and to develop the subject of geometrical isomerism as found in ring formations. This isomerism is not limited to the benzene series, but is capable of a more general application. According to von Baeyer, *all* rings have the carbon atoms in a plane, and the connected radicals may lie on the same or on opposite sides of that plane. The simplest ring known is cyclopropane,

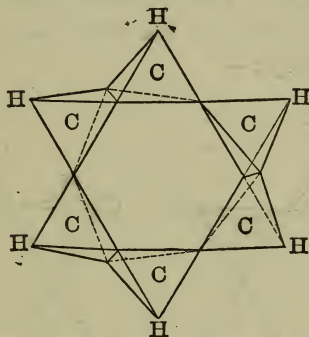


which shows the isomerism which might be expected from von Baeyer's views.

<sup>1</sup> Lieb. Ann. d. Chem. 269, 145.



Another illustration of geometrical isomerism in benzene derivatives may be found in benzene<sup>1</sup> hexachloride. Two isomeric hexachlorides have been found, differing in physical properties and in stability, the  $\beta$  variety being much more stable than the other. Friedel discusses these bodies by applying van't Hoff's hypothesis to Kekulé's plane formula, and pictures the benzene molecule as made up of three pairs of tetrahedrons, the *pairs* being joined together by a common apex, and the individuals of each pair being joined together by a common edge, giving the following figure:—

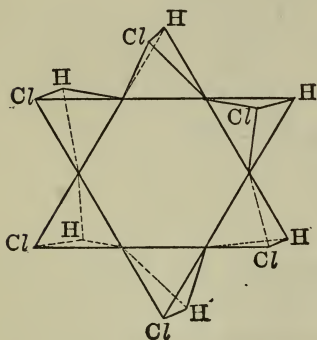


Upon formation of the hexachloride, the double bonds, represented by edges, are broken, and there may be formed a molecule, in which the chlorine atoms are all on the same side of the plane of the carbons, giving the *cis* isomer; or four of the chlorine atoms may be on one side and two on the other, giving the *trans* isomer, as pictured below.

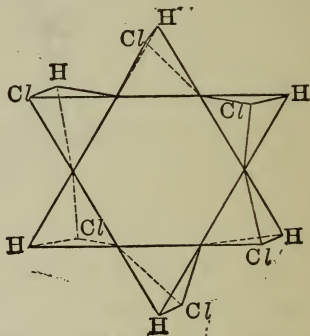
Friedel judges that the *cis* molecule is the  $\beta$  or more stable modification, thinking that the greater symmetry of this molecule may account for the comparative stability, greater den-

<sup>1</sup> J. Chem. Soc. 60, 165; Bull. Soc. Chem. (3) 5, 130.

sity, and higher boiling-point of the  $\beta$  hexachloride. Friedel also finds a connection between the symmetry of the molecular formula and that exhibited by the crystallized substance. Thus the  $\alpha$  hexachloride crystallizes in the monoclinic system, and a study of the formula suggested by Friedel shows that the *trans* molecule has one and only one plane of symmetry. The  $\beta$  variety has been described as crystallizing in regular octahedrons, but Friedel finds that these crystals affect polarized light, and upon careful study decides that these octahedrons are formed by grouping together eight triangular pyramids belonging to the hexagonal system, and the figure shows that the molecule of the *trans* hexachloride possesses hexagonal symmetry:—



*Cis* hexachloride of benzene.



*Trans* hexachloride of benzene.

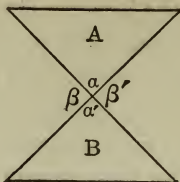
Friedel's discussion is very interesting; but it has already been pointed out that any stereo-arrangement of the benzene nucleus must at present be accepted with caution. Kekulé's formula, however, appears from these discussions to be well adapted to being brought into harmony with the tetrahedral symbolism used in the other series of organic compounds.



Another formula for the benzene ring has been devised by Sachse,<sup>1</sup> who has also adopted the tetrahedron as the geometrical figure for each carbon atom. He states that if the carbon atoms in the formulas of Kekulé, Ladenburg, or Claus be replaced by tetrahedrons, figures result which are not in complete accordance with the facts observed, and particularly in that they offer no explanation of the fact that *six* tetrahedrons form the most stable possible combination, and that in the union of two benzene rings in their most stable form, as in naphthalin and anthracene, there are two carbon atoms common to the two rings. These facts he thinks are explained perfectly by his own geometrical mode of representation; and as there are some very interesting points about his formula, it may be worth while to consider it briefly here.

His geometrical formula is derived by taking away any two parallel faces from the regular octahedron, and placing upon each remaining face a tetrahedron whose face equals the face of the octahedron. The resulting figure has then six free, solid angles, one from each tetrahedron, representing the points of attachment for the six hydrogen atoms. An examination of the figure shows that three valencies from each carbon atom are so taken up by the neighboring carbons that a normal union of another element through these affinities cannot take place without changing the entire system. This six-membered ring is then the most stable of all ring formations, because each atom is so combined with its neighbor that it is in stable equilibrium, and any motion in the molecule must be a motion of the molecule as a whole, any periodic oscillation of the separate atoms being impossible. This is proved geometrically as follows:—

<sup>1</sup> Ber. 21, 2530.



If A and B represent the projection on the plane of the paper of two tetrahedrons joined by double bonds, according to the common mode of representation following van't Hoff's hypothesis, then to be in equilibrium,  $\beta$  must equal  $\beta'$ , and

$$\beta = \beta' = \frac{360^\circ - 2a}{2}$$

in which  $a$  equals the regular tetrahedral angle,  $70^\circ 32'$ ,  $\therefore \beta = 109^\circ 28'$ , which is the interfacial angle of the regular octahedron. Now, since the inside of our molecule is an octahedron, it follows that  $\beta = \beta'$  for each pair of tetrahedrons, and that they are all, therefore, in a state of stable equilibrium.

Again, since  $\beta = \beta'$ , one of these angles being opened inward toward the centre of the octahedron, and the other outward, it becomes possible for this exterior angle to become the interior angle of another ring exactly like the first, and these two rings will have two carbon atoms in common, and this would seem to be the most stable possible way of combining two rings. This, then, explains the constitution of such bodies as anthracene and naphthalin, for only in this way, keeping two carbon atoms in common, is it possible for both rings to retain at the same time the form of the most stable of all systems.

The main peculiarity of this conception of the benzene ring is that we have here only double linkage, each atom being doubly bound to two other carbon atoms, — a state of affairs

which would generally be considered impossible, since it would leave no place for the hydrogen atoms. To account for this, the author introduces a new conception of the union of carbon atoms with each other, peculiar to benzene and other rings. He assumes that when two carbon atoms are combined by double linkage, there is not a complete neutralization because the valencies meet at an angle. Hence a third valency from a third carbon atom is used in completing the mutual neutralization. Therefore, whenever three carbon atoms meet in one point on the model, there is this distribution of affinities which is peculiar to ring formations, and particularly to benzene.

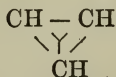
Sachse<sup>1</sup> has also offered a formula for hexamethylene, which can easily be derived from his formula for benzene, and which shows the relation between the two bodies.

Sachse's geometrical formula for benzene possesses the advantages claimed for it in explaining the facts mentioned. It also shows a possibility of two kinds of double linkage, the ordinary loose kind in which the saturation is incomplete, and this more stable form in which complete saturation is effected by the presence and action of a third carbon atom. In this conception, the six atoms forming the benzene nucleus are not in a plane; as they are in von Baeyer's theory, and in some ways this commends itself. The fact that the hexa compounds are generally more stable and more easily formed than the penta is certainly an argument against von Baeyer's theory, and that theory offers no explanation of the stability of the double bonds which must be present. On the other hand, in the present state of our knowledge regarding the nature of atoms and valence, it is as difficult to grasp the idea that the bonds of affinity do not completely saturate each

<sup>1</sup> Ber. 23, 1363.

other because they meet at an angle, as it is to comprehend von Baeyer's "strain" theory.

It has also been urged against Sachse's formula that, on the same principle, a number of other bodies ought to be capable of existence which have never been discovered; for example, such a body as that represented by the following formula:



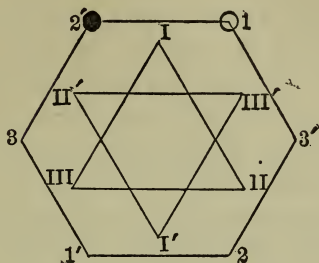
The non-existence or non-discovery of certain particular bodies is, however, a weak argument against any hypothesis, and Sachse's three-dimension formula for benzene must be considered an interesting and ingenious theory, even though the time may not seem quite ripe for adopting any such formula at present.

Another geometrical formula which has been suggested for the benzene nucleus is that offered by Herrmann,<sup>1</sup> and this seems to have its origin entirely in theoretical speculations. For hexahydrobenzene, he adopts the figure of the regular hexahedron, having the six carbon atoms in the centre of the faces, and the twelve hydrogen atoms in the middle points of the edges. These hydrogen atoms are divided into two sets, and one set is taken away in the formation of benzene. This leaves, as the geometrical form for benzene, the figure of an octahedron inscribed in a cube, the six carbon atoms occupying the angles of the octahedron, and the six hydrogen atoms the centres of six of the edges of the cube, arranged in such a way that if one edge contains a hydrogen atom, the edge opposite contains none.

The plane of the hydrogen atoms is not a plane of symmetry, but by projection of the places of the carbon atoms

<sup>1</sup> Ber. 21, 1949.

upon this plane, the following figure is obtained, in which the Roman numerals represent the carbon atoms : —



I, II, and III lie *over*, and I', II', and III' *under*, the plane of representation, and the configuration possesses six planes of symmetry. Adopting this formula, if two hydrogen atoms are replaced by two different radicals, we may get two configurations bearing to each other the relation of object and reflected image, as is shown by allowing 1 and 2' to exchange places in the above figure. Analogy would lead us to expect optical activity in such a case, but no such activity has been observed in any normal benzene derivative. Herrmann meets this criticism upon his formula by supposing that the plane of the hydrogen atoms, though not a geometrical, is an optical plane of symmetry, and that the rotation which the plane of polarization of the light ray entering the molecule suffers through the influence of one system of atoms is removed by the action of the equal and oppositely placed system on the other side of the plane.

The speculations of Herrmann, it will be observed, are based entirely on geometrical reasoning, and he makes no assumptions whatever in regard to the nature or valence of the atoms, being occupied entirely with their geometrical distribution.



Such formulas as these are interesting principally as showing the kind of work which is being done, and the speculations which are being offered in stereo-chemistry. Perhaps they show also, that there is some danger of pushing stereo-chemical ideas too far and too rapidly. So many of these ideas have their basis in well-grounded facts that it would be a pity to cast valuable and helpful suggestions and symbols into disrepute by a rash and definite picturing of molecules, without sufficient grounds. While all of these geometrical representations of the benzene nucleus are interesting, in so far as they help to explain the properties of bodies, great caution should be used in adopting any one of them.

## IV.

### THE STEREO-CHEMISTRY OF NITROGEN.

It has been shown in the foregoing chapters that carbon compounds are capable of exhibiting two different kinds of isomerism, which agree in this particular, that such isomeric forms possess the same structural constitution, and can only be explained on the assumption of a different configuration of the atoms in space. These two kinds of isomerism have been defined as physical and stereo-chemical.

More recently there has been an effort to carry over the ideas of the stereo-chemistry of carbon to other elements, notably nitrogen, and some cases of isomerism have been observed in nitrogen compounds inexplicable on the structural theory, which seem to justify this attempt. It is noticeable, however, that such cases of isomerism have always been observed in *organic* compounds containing nitrogen.

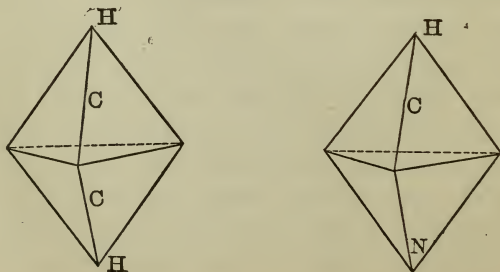
The nitrogen atom differs essentially from the carbon, in that it has a varying valence. The vast preponderance of the compounds, which can be explained on the supposition that carbon has a valence of IV, will perhaps justify this statement, though neither van't Hoff's nor any other theory offers a thoroughly satisfactory explanation for such a body as carbon monoxide. But nitrogen differs essentially from carbon, in that compounds of both triad and pentad nitrogen are of common occurrence. This at once brings before us several



very difficult questions. Are these two kinds of valencies of equal or unequal value? Do they all act in the same plane, or are they like the valencies of carbon distributed in space, and how is it possible for us to represent by any geometrical figure an atom with variable valence? These are questions, none of which, perhaps, can be answered to our entire satisfaction in the present state of our knowledge, but they are very suggestive of thought.

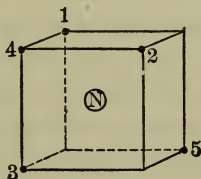
Whatever may be said in answer to the question of the equality or non-equality of the five nitrogen bonds, it must be conceded that they differ in one essential, three are necessarily active in all compounds, the other two may be dormant. If we endeavor to get a three-dimension formula for the nitrogen atom, it would seem to be necessary to suppose that the valencies are *not* all equal, since it is impossible to find a symmetrical arrangement of five points in three-dimension space.

Although carbon itself differs widely from nitrogen, the CH group seems to be replaceable by nitrogen in a number of compounds; for example, acetylene,  $\text{CH} \equiv \text{CH}$ , corresponding to hydrocyanic acid,  $\text{CH} \equiv \text{N}$ , and pyridin,  $\text{C}_5\text{H}_5\text{N}$ , to benzene,  $\text{C}_6\text{H}_6$ . This has given rise to the suggestion that such corresponding molecules may have corresponding configurations, as shown by the following figures:—



In such a conception as this, the triad nitrogen is pictured as having its valencies in three of the angles of a tetrahedron, whose fourth angle is occupied by the nitrogen itself. In this case it is evident that the three valencies do not lie in the same plane; and a careful study of many nitrogen compounds has led some investigators to conclude that, though in certain compounds the three valencies all work in the same plane, in others they are bent from that position.

Van't Hoff<sup>1</sup> was the first to suggest a three-dimensional arrangement of the radicals attached to the nitrogen atom. According to him, the radicals attached by the three valencies which are always active must lie at equal distances from the nitrogen atom. The other two valencies differ from these in that they may be dormant, and from each other in that one holds preferably negative, the other positive, atoms or radicals. In any geometrical figure to represent these facts, indicating the first set of valencies by 1, 2, and 3, and the second by 4 and 5, each of the latter should be equidistant from 1, 2, and 3. The form suggested by van't Hoff is a cube, in which the nitrogen occupies the centre, and which is represented by the accompanying figure.

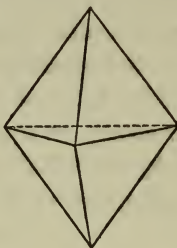


Lossen has discovered certain hydroxylamine derivatives, which, though they *may* be explained on the ground of structural differences without any serious inconvenience, seem to

<sup>1</sup> Ansichten ueber organische Chemie, p. 79.

van't Hoff to be explained more naturally on the assumption that there are three different kinds of hydrogen atoms in hydroxylamine. He would, then, write the formula for this latter body,  $\text{NO} \cdot \text{H}_3$ , and, using the geometrical formula given above, the oxygen may be assumed to occupy places 1 and 2, whereby there are left for the three hydrogen atoms only places 3, 4, and 5, no two of which are alike in their relations to the other atoms.

Similar attempts to determine a three-dimensional formula for the nitrogen atom have been made by Willgerodt,<sup>1</sup> and by Burch and Marsh,<sup>2</sup> who were apparently ignorant of van't Hoff's work in this direction, and who pictured the nitrogen as a double tetrahedron.



They attempt to reconcile the varying valence of nitrogen with this conception by supposing that two atoms of nitrogen, in their apparently triad condition, may combine with one another by their two available affinities to form a condensed molecule, and that such molecules are readily dissociated by heat into the ordinary molecules containing *quasi* triad nitrogen. Experiments with ethylamine vapor seemed to show that, to some extent at least, this vapor breaks up, when

<sup>1</sup> J. pr. Chem. [2], 37, 449; 41, 291, 526.

<sup>2</sup> J. Chem. Soc. 55, 656.

heated from  $17^{\circ}$  to  $100^{\circ}$ , into a larger number of molecules. According to this view, the valence of the nitrogen is essentially V, and when found with apparently a valence of III, we are dealing with molecules which have been dissociated, and in which the two available bonds are too feeble at the temperature of observation to enable the two molecules to hold together.

They assume, also, that different elements have different effects in weakening or strengthening these two bonds. Thus, that oxygen strengthens and hydrogen weakens these bonds is inferred from the fact that  $\text{NH}_3 = \text{NH}_3$  and  $\text{NH}_4 - \text{NH}_4$  are non-existent, whereas  $\text{NO}_2 - \text{NO}_2$  is well known. They suggest that the union of an element of strong affinity with one of the valencies might render the other four equal toward atoms of weaker affinities; for example, representing  $\text{N}^{\vee}$  by the double tetrahedron as above, if one angle is taken up by chlorine, the remaining four are symmetrical with reference to one point in the molecule, and may be satisfied by four equal atoms, as in  $\text{NH}_4\text{Cl}$ . These speculations are ingenious and interesting, especially in their explanation of varying valence, but seem hardly sufficient to justify us in adopting any three-dimensional formula for the nitrogen atom at present.

In studying the cases of nitrogen compounds in which either of the kinds of geometrical isomerism observed in carbon compounds is conceivable or has been found, it may be well to consider them under the following heads: —

I. Compounds in which nitrogen exhibits single linking.

(a) Triad nitrogen.

(b) Pentad nitrogen.

II. Compounds in which nitrogen shows double linking.

(a) Doubly linked to carbon.

(b) Doubly linked to nitrogen.

Under I. (*a*), in case the nitrogen is combined with three different radicals, giving the general formula,



it is conceivable, as has been before shown, that the nitrogen should take the place of CH in a tetrahedron, giving an arrangement capable of existing in two forms, one of which should be the reflected image of the other. This should give rise to a physical isomerism, manifested, as in the case of compounds containing asymmetric carbon, by optical activity. All efforts, however, to discover optical activity in bodies of this general formula have proved unavailing, therefore it is generally conceded that the three valencies in bodies of this type lie in a plane, making geometrical isomerism impossible.

I. (*b*) Compounds containing pentad nitrogen with single linking.

No optical activity has been observed in compounds of this class except in cases where no two of the radicals combined with the nitrogen are identical; that is, in bodies of the general type,



Le Bel has succeeded in obtaining methyl-ethyl-propyl-isobutyl-ammonium iodide in active form,<sup>1</sup> and from this also other salts with the same power, but with great instability. Very few such cases are known, but they are sufficient to indicate that, in the completely asymmetric nitrogen molecule, there

<sup>1</sup> Compt. rend. 112, 724.



is the capability of the same kind of isomerism as that exhibited in a molecule containing asymmetric carbon. It has been suggested that, in these cases, the  $(\text{Nx}^{\text{I}})^{\text{IV}}$  being equivalent to  $\text{C}^{\text{IV}}$ , the four valencies of this group may be distributed in space in the same way as in the carbon atom, and therefore there may be a possibility of the same kind of isomerism.

These are probably the only compounds yet known in which optical activity is not connected with the presence of asymmetric carbon, but the existence of these compounds is in complete accordance with Le Bel's statement of the fundamental principle of stereo-chemistry: "If a substance is derived from the primitive type  $\text{MA}_4$ , by the substitution of three different atoms or radicals for  $\text{A}_3$ , its molecule will be asymmetric and will possess the power of rotation." In this, M stands for any radical simple or complex, so there is nothing in this form of statement which would limit the power of causing rotation to a single carbon atom, to which four different radicals are attached. As a matter of fact, however, the phenomenon is almost universally met with in these latter compounds, so that the two forms of stating this fundamental principle of stereo-chemistry, van't Hoff's and Le Bel's, have frequently been considered identical.

In addition to these optically active nitrogen compounds, Le Bel has observed *dimorphism* in trimethyl-isobutyl-ammonium chloride,<sup>1</sup> which he attributes to stereo-isomerism, and the same phenomenon has been observed by Schryver and Collie in methyl-ethyl-pentyl-ammonium chloride.<sup>2</sup> Tri-ethyl-benzyl-ammonium iodide is another body which is apparently capable of existing in different isomeric forms, according to the order in which the hydrocarbon radicals are combined

<sup>1</sup> Compt. rend. 110, 144.

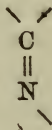
<sup>2</sup> Chem. News. 63, 174.



with the nitrogen,<sup>1</sup> and of this van't Hoff says, "These isomers may certainly be due to a difference in the value of the nitrogen affinities, but may equally be due, and this is, perhaps, the more natural assumption, to a different arrangement in space of the groups combined with the nitrogen."

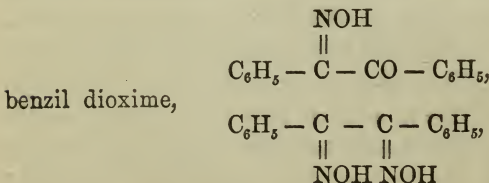
II. (a) Compounds containing nitrogen joined by double bonds to a carbon atom.

This is by far the most important class of nitrogen compounds in which geometrical isomerism has been observed. In bodies of the type,



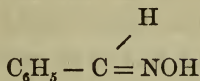
an isomerism has been quite commonly detected which is very closely related to the stereo-chemical isomerism observed in doubly linked carbon compounds. Such geometrical isomers differ in all their physical properties, and in those chemical properties which depend on inter-molecular reactions, the different distance of the atoms from each other, etc.

This kind of isomerism is almost entirely limited to oximes and their derivatives, but has also been observed in some ethers of hydroxamic acids and in some hydrazones. The principal oximes studied are benzil monoxime,



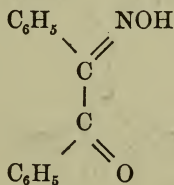
<sup>1</sup> Ber. X., 45, 309, 561, 964, 1152, and 1634.

and benzaldoxime,



Two different benzil dioximes were first discovered by Victor Meyer and Goldschmidt; and the structural identity of these two bodies was proved by V. Meyer and Auwers,<sup>1</sup> who later also discovered a third isomeric form with same structure as the other two.<sup>2</sup> The two isomeric benzil monoximes have also been carefully studied, and proved to be structurally identical by Auwers and Meyer,<sup>3</sup> and by Auwers and Dittreich.<sup>4</sup>

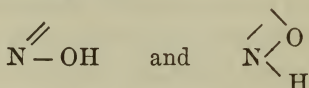
The principal properties of the two benzil monoximes which are of importance in this discussion are as follows: They are both formed from benzil,  $\text{C}_6\text{H}_5 - \text{CO} - \text{CO} - \text{C}_6\text{H}_5$ , and hydroxylamine at the ordinary temperature. Both are decomposed by hydrochloric acid into benzil and hydroxylamine. They combine further, even at ordinary temperatures, with hydroxylamine, and produce two different dioximes. Both combine with phenyl hydrazin to form hydrazones, and the presence of carbonyl in both is established beyond doubt. They are both optically inactive. To each belongs the structural formula



Here we have, then, a case of isomerism clearly similar to the stereo-chemical isomerism of organic bodies, and yet with

<sup>1</sup> Ber. 21, 784.    <sup>2</sup> Ber. 22, 705.    <sup>3</sup> Ber. 22, 537.    <sup>4</sup> Ber. 22, 1996.

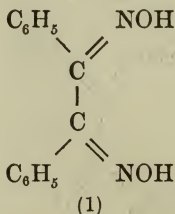
no double linking between the carbon atoms. According to the theories before given, there should be no possibility of isomerism in a body of this type unless due to structural differences. Experiments done with other bodies containing an NOH group had shown that there were two possible arrangements inside this group,



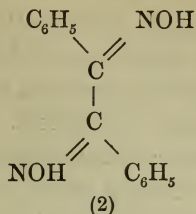
Experiments by which the latter group had been proved present in some compounds were carefully repeated by Auwers and Dittreich, who proved conclusively that in this case both isomers contained the same group,



In the dioximes the conditions are very similar to those in the monoximes, only that we have here *three* different bodies, all of which must be conceded, after the careful investigation of Auwers and Meyer, to be represented by the same structural formula:—



This isomerism, then, is not to be explained structurally, nor by space configurations according to van't Hoff's theories, for if we should write the formula as follows,



(2) could be derived from (1) by simple rotation of a carbon atom, and should, therefore, according to van't Hoff, represent the same isomeric form.

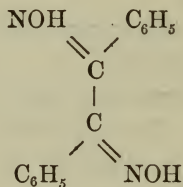
In explanation of this remarkable phenomenon, various theories have been advanced.

I. Theory that this isomerism may be due to the inequality of the nitrogen bonds. This hypothesis has hardly been sufficiently developed to be dignified by the name of *theory*. Van't Hoff, without discussing the subject of the nitrogen compounds in detail, merely offers this suggestion as a possible explanation. He says: "We do not know the nature of the union of the carbon atoms with the NOH groups, but it is quite possible that the two bonds which effect the union are of unequal value. Hence the two carbon atoms will be asymmetric, and without being deprived of free rotation, will give rise to two isomers, inactive and analogous to racemic and mesotartaric acids."

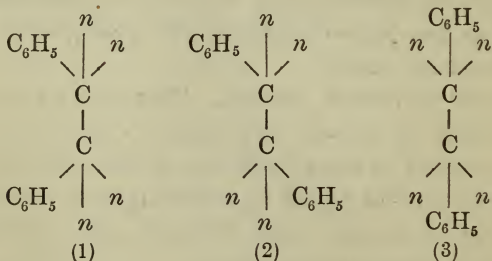
II. Theory of limited rotation. This is the theory which was developed by Auwers and Meyer. These two eminent chemists differed in some details as to the ultimate *cause* of the phenomenon, but agreed in assuming that in some cases there might be two or more different *stable* arrangements around singly linked carbon atoms.

In 1888, the two then-known benzil dioximes were carefully studied by Auwers and Meyer, who showed that they were

structurally identical, and that no theory had ever been brought forward which would account for such isomeric bodies. The explanation which they proceeded to offer was a modification of van't Hoff's second hypothesis. While they acknowledged that the principle of free rotation was to be accepted for the vast majority of singly linked carbon compounds, they assumed that there might be exceptions to this rule. For the benzil dioximes, accepting van't Hoff's hypothesis, there should be only one configuration possible,



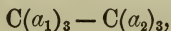
On the other hand, assuming that the different configurations produced by the rotation of one of the carbon atoms represent different isomeric modifications, there would be a possibility of three different forms shown by the following formulas, in which the group NOH is represented by  $n$ : —



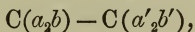
At the time when these speculations were offered, only two of these dioximes were known, but in the following year, a

third isomer was discovered by Auwers and Meyer, who felt that their theory received great support from this discovery. This third isomer, the  $\gamma$  benzil dioxime, is characterized by its instability, slight heat under all circumstances changing it to the  $\beta$  form, and by its tendency to form an anhydride, therefore formula (1) was assigned to it; but it would be impossible to decide which of the other formulas belonged to each of the other two forms. Hantzsch argued that (2) and (3) would not represent the comparative properties of the  $\alpha$  and  $\beta$  forms satisfactorily. It might be expected that their properties would be closely similar, and that they would differ only as right and left tartaric acids, but this is not found to be the case. Leaving other properties out of consideration, there is a much greater difference in stability than might be expected from these formulas, the  $\beta$  variety being considerably more stable than the  $\alpha$ .

A second assumption made by Meyer and Auwers is free from this objection, and is yet based on similar ideas. They assumed that in the system

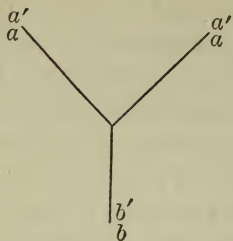


two positions of stable equilibrium might be reached, one when the combining radicals were in the same vertical line, and the other when they were midway between these positions. Then for

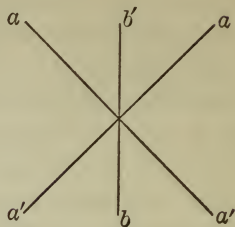


configurations are shown by Auwers to be possible, represented to an observer looking from above upon the molecule by the following symbols:—

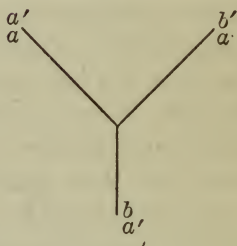
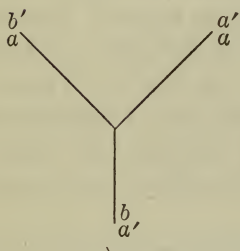




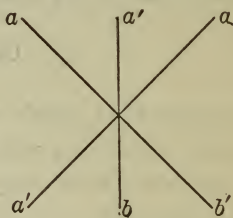
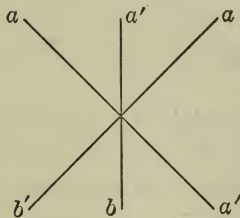
(1)



(2)



(3)



(4)

(3) and (4) represent pairs of enantiomorphous configurations, which may be considered identical. On this assumption, there were shown to be four possible configurations. This was open to the objection that only three isomers had been discovered; and though this was only negative evidence, their

position would have been greatly strengthened if a fourth form had been obtained.

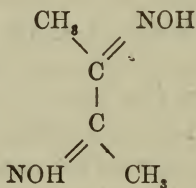
In 1890, Robert Behrend<sup>1</sup> published an article on the stereochemistry of nitrogen compounds, in which he refers their configuration to electrical polarity. He assumes, for example, that ammonia has a positive and a negative pole, corresponding to the two dormant bonds. If now, two atoms of hydrogen be replaced by other radicals, their position will be necessarily fixed by their electrical character. His ideas in regard to the configuration of the monoximes and dioximes agreed with those of Auwers and Meyer, but whereas, heretofore, the reason for the grouping of the system had been found in the carbon atoms, he found it in the directive working of the radicals attached to the carbon.

Auwers, in his later ideas as set forth in the "*Entwicklung der Stereochemie*," differed somewhat from Meyer as to the fundamental cause for these stable configurations. Meyer assumed two different kinds of single union between carbon atoms, only one of which, by far the most common kind, allows unhindered rotation. He arrived at this conclusion from some very interesting speculations made by himself and Riecke<sup>2</sup> concerning the nature of the carbon atom. Auwers, on the other hand, thinks that two singly linked carbon atoms are rotatable under all circumstances; that at the instant of formation of a molecule, rotation begins, but is quickly checked by the directive affinities of the atoms, and goes over into an oscillatory motion around a position of equilibrium; finally, that in each case it depends on the chemical nature of the combining radicals whether only one or several positions of equilibrium can have a lasting existence in the form of isomeric modifications. Auwers agrees with Behrend in con-

<sup>1</sup> Ber. 23, 454.

<sup>2</sup> Ber. 21, 946.

sidering the electrical character of the radicals combined with carbon as of great importance in determining whether only one or several stable positions of equilibrium are possible. In case the radicals are all of nearly the same electrical character, as in the oximes, he thinks several such positions are possible, whereas, if there is a marked difference in electrical character, the positive and negative radicals will tend to draw as near together as possible and give only one form. As an illustration of this, he points to dimethyl glyoxime,

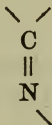


which exists in only one form, according to his theory on account of the fact that methyl is more positive than benzil, and therefore has a stronger attraction for the NOH group, while, on the other hand, he finds that many derivatives of benzil behave, in regard to oxime formations, exactly like benzil itself.

These theories, it will be observed, all explain the observed phenomenon by reference to the *carbon* rather than the *nitrogen* atoms, and demand for certain cases an exception to van't Hoff's second hypothesis, which states that all configurations which can be derived from each other by simple rotation of one carbon atom, must be considered identical. In this explanation of the isomerism of the oximes, no special stress is laid upon the nitrogen atoms except that attention is called to the fact that the NOH group is of much the same electrical character as  $\text{C}_6\text{H}_5$ . A similar isomerism might then be expected

in singly linked carbon compounds containing no nitrogen, but radicals of nearly the same electrical character. It has already been mentioned that an isomerism has been observed in the benzil carbonic acids and a very few other compounds which Meyer would explain, as in the case of the oximes, on the supposition of limited rotation. *Very* few such bodies are, however, known with certainty. Undoubtedly, if careful study in the future should result in the knowledge of well-authenticated cases of singly linked carbon compounds containing no asymmetric carbon and no nitrogen, and yet exhibiting an isomerism incapable of explanation from structural differences, it would be a strong support to the Auwers and Meyer theory.

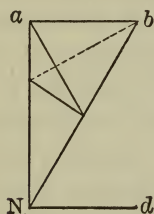
One more theory remains to be mentioned, that of Hantzsch and Werner, which was advanced in 1890, and which refers the isomerism of the oximes and similar bodies containing nitrogen doubly bound to carbon, to the stereo-arrangement of the groups combined with the nitrogen.<sup>1</sup> They assume that bodies of the type



can exhibit a geometrical isomerism entirely analogous to that shown in bodies of the  $>\text{C}=\text{C}<$  type, and that this isomerism is due to the fact that in these compounds the three valencies of the nitrogen atom do not all lie in the same plane, one being drawn out of the plane of the other two by the attraction of other atoms or radicals in the molecule. According to this view, as has been already intimated, the nitrogen atom may be pictured as lying in one of the solid

<sup>1</sup> Ber. 23, 11, and Grundriss der Stereo-chemie.

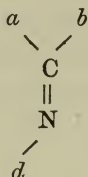
angles of a tetrahedron, and exerting its affinities in the direction of the three edges. Then, whenever a nitrogen atom is united to carbon by two bonds, a possibility of isomerism would exist, as shown by the following figures:—



and



or,

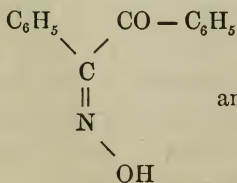


and

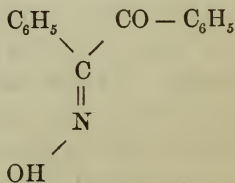


According to this view, the valency attaching *d* to *N* is turned from the plane of the other two by its attraction either for *a* or *b*.

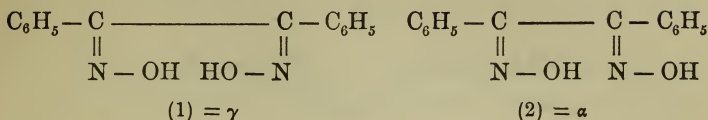
They would then explain the isomerism observed in benzil monoxime by the formulas:—



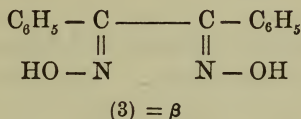
and



and for the benzil dioximes: —



and



For the three latter isomers, he assigns the formulas as indicated above, giving (1) to the least stable form, which readily goes over into its anhydride, and assuming that (3) would represent the configuration most favorable for stability.

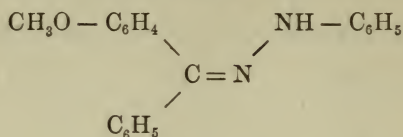
The principal objections brought by Hantzsch and Werner against the theory of Auwers and Meyer were as follows:—

1. It does not express the parallelism between the stereo-isomeric carbon and stereo-isomeric nitrogen compounds. A number of compounds are known, including the oximes and their derivatives, which contain nitrogen, doubly linked to carbon, and which exhibit an isomerism closely similar to that shown by doubly linked carbon compounds. Hantzsch and Werner assign to such bodies formulas which show this analogy, whereas Meyer and Auwers throw it back upon singly linked carbon atoms, and the parallelism is entirely lost.

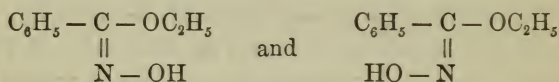
2. The theory of Auwers and Meyer can only be applied to compounds in which the carbon atom, attached by two bonds to nitrogen, is also connected with another carbon atom. It therefore leaves out of account several bodies whose isomerism is plainly of the same kind as that which their theory



seeks to explain. It offers no explanation for the isomerism of the hydrazones; such bodies, for example, as



which are explained by Hantzsch and Werner on exactly the same principle as the oximes. Also two different ethyl hydroxamic acids have been discovered by Lossen, unaccountable on the structural theory, and not to be explained by the theory of Auwers and Meyer, but given by Hantzsch and Werner the following formulas:—

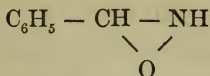


In this connection, the benzaldoximes have received the greatest attention. If these two bodies can be proved to be structurally identical, it would be almost irrefutable evidence against the Meyer and Auwers theory, since they are so closely related to the other oximes that any theory which would account for one on space relations should also include the other; and yet their formula,  $\text{C}_6\text{H}_5-\text{CH}=\text{NOH}$ , would exclude the application of the theory of limited rotation of singly linked carbon atoms.

The iso-benzaldoxime was discovered by Beckmann<sup>1</sup> in 1889, and after a careful study of its reactions, he was led to give it the formula<sup>2</sup>

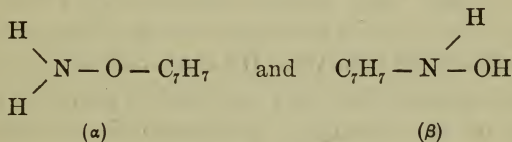
<sup>1</sup> Ber. 20, 2766.

<sup>2</sup> Ber. 22, 429, 514, 1531, 1588; 23, 1680.

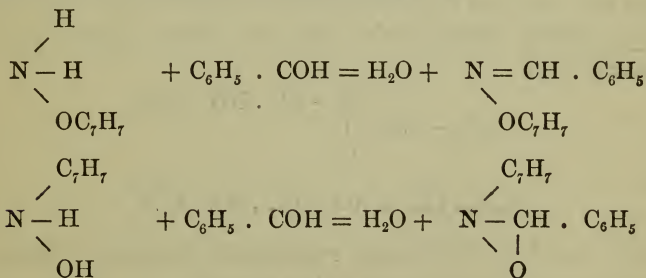


The reactions which led him to the conclusion that the two benzaldoximes were structurally different were the following:—

1. The benzyl ethers of the two oximes, by heating with hydrochloric acid in presence of benzaldehyde, give two different benzyl hydroxylamines. Behrend and Leuchs<sup>1</sup> showed that these last compounds have different structures, which correspond to



2. Conversely, by action of these two different benzylhydroxylamines on benzaldehyde, he found that he could synthetically produce the benzyl ethers of the two benzaldoximes, reactions which he expressed as follows:—



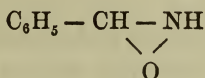
3. The benzyl ethers of the two benzaldoximes showed a characteristically different behavior under action of concen-

<sup>1</sup> Ber. 22, 613.

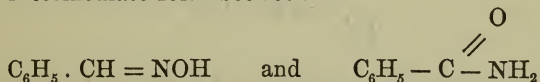


same ether from the normal and iso-oximes, and he concludes that in Beckmann's experiments, the presence of water may have had a disturbing effect upon the smooth, plain course of the reaction.

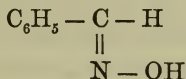
Hantzsch and Werner<sup>1</sup> argue that the formula



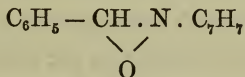
is untenable for iso-benzaldoxime, because that would seem to be an intermediate form between



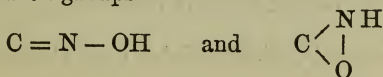
and according to this, the iso-oxime should be easily changed into benzamide, while, on the contrary, it may be directly decomposed into water and benzo-nitrile, which is in direct accordance with their space formula:—



They also urge that the finding of an ether of formula

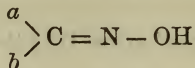


does not necessarily prove the pre-formed existence of the imido group in iso-benzaldoxime. They think that the oximes in general may be tautomeric bodies, reacting in the sense of two formulas with groups

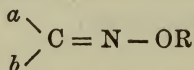


<sup>1</sup> Ber. 23, 1243.

so that from each of the two benzaldoximes, an ether of either formula may be prepared, but that the normal and iso-oximes in general both possess the structural formula,



is proved by the fact that all plain reactions carried on under absolute exclusion of water give without exception derivatives of the structural formula



Meanwhile, the strife in regard to the oximes is still raging. Claus<sup>1</sup> and Nef<sup>2</sup> are strenuously opposed to the consideration that the oximes in general have been proved to be structurally identical, although so many facts seem to point in that direction. Auwers, Meyer, and Beckmann admit the structural identity of most of the oximes, but make an exception in the case of benzaldoxime, while Hantzsch, Werner, Goldschmidt, and others consider it proved that these bodies are also structurally identical, although they may react as tautomeric bodies.

Granting the structural identity of the benzaldoximes, the explanation of isomeric oximes on the theory of limited rotation falls to the ground. On the assumption that they are structurally different, the Auwers and Meyer theory might stand for the other oximes, but even then, Hantzsch's explanation would seem in better accordance with the number and properties of the isomeric forms observed, and to explain on

<sup>1</sup> J. für prak. Chemie [2], 44, 315; 45, 1, 377; 46, 34, 546, 556; 47, 267; 48, 80.

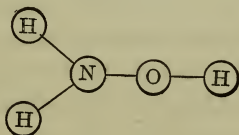
<sup>2</sup> Liebig's Annalen der Chemie, 270, 325.



one principle the isomerism of a larger number of compounds, without necessitating any exception to the van't Hoff hypothesis, which is found to be true in such a vast majority of cases; and therefore the Hantzsch and Werner theory seems most worthy of acceptance.

Auwers and Meyer themselves, in 1890,<sup>1</sup> accepted as valid the criticisms on their former theory, and declared their supposition of limited rotation untenable as an explanation of the isomeric nitrogen compounds. This decision was hastened by the discovery of certain structurally identical ketoximes which contained no singly linked carbon atoms, and which therefore could not be explained on their old theory. Among these were the oximes of parachlor-benzo-phenone,  $C_6H_5-CO-C_6H_4Cl$ , discovered by Auwers and Meyers themselves.<sup>2</sup>

They were, however, still unwilling to accept the theory of Hantzsch and Werner, and referred the phenomenon instead to a stereo-isomerism of the oxygen atom. Their argument was that their opponents had endeavored to explain a phenomenon found only in hydroxylamine by reference to a property of the nitrogen atom, and they could not therefore understand why a similar isomerism had not been found in derivatives of ammonia and in azo and azoxy bodies. So long as such were wanting, they concluded that the cause of the phenomenon should be found not in the nitrogen atom, but in the  $NH_2OH$  group. The formula for this is generally written as follows:—

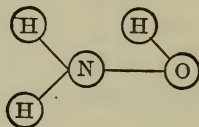


<sup>1</sup> Ber. 23, 2403.

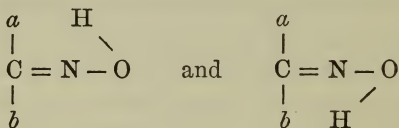
<sup>2</sup> Ber. 23, 2063.



They assumed, however, that the valencies of the oxygen, like those of all other atoms, could be bent from their normal direction, and that the hydrogen of the hydroxyl would take a position compelled for it by the attraction both of the oxygen and nitrogen; that is, a position between these two atoms. It is kept from drawing nearer to the nitrogen atom in a straight line by the oxygen which lies between, and therefore will assume the position represented in the following formula, in which it is assumed that the hydrogen of the hydroxyl is not in the plane of the paper: —



The formulas for the two oximes would then become

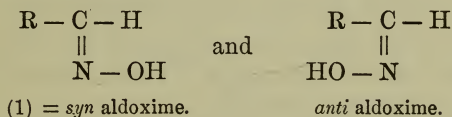


In order that these formulas should represent two different isomeric forms, it is evident that the hydrogen atom must be assumed to be incapable of free rotation around the oxygen atom, and one naturally asks the reason for such an assumption.

New discoveries are meanwhile constantly increasing the number of isomeric forms which can be explained by Hantzsch's hypothesis, although it is true that most of these bodies are such as may be considered as derivatives of hydroxylamine, including the aldoximes and aldoxime carbonic acids, ketoximes, dioximes, and the derivatives of hydroxamic acid.

In these compounds, the change of one isomer to the more stable form takes place usually under the influence of heat, but sometimes gradually of itself at ordinary temperatures, and quite commonly under chemical influences. If the rise of temperature goes on to the decomposition of the molecule, the same decomposition products are formed from each isomer. In these respects the oximes are closely analogous to the ethylenic bodies, and this analogy is shown by Hantzsch's formula.

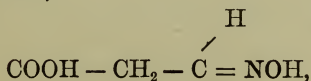
The aldoximes are of two kinds, — those which decompose easily into water and a nitrile, and those which do not undergo this decomposition. These forms are explained by Hantzsch's formulas as follows : —



The stability is much influenced by R. In the fatty kingdom, the *syn* aldoximes are almost the only ones capable of existence, while in the benzene series the *anti* prevail. In cases where only one isomeric form is known, this one corresponds to one or the other of the classes named above, and it is supposed that its stereo-isomeric modification is too unstable to have a lasting existence. This stereo-isomerism is very common in the aromatic series, but has been observed in only a few of the fatty derivatives; e.g., in the aldoxime,

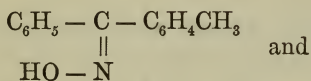


in aldoximacetic acid,

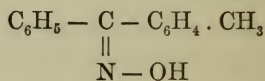


and in a few other compounds recently described by Dunstan and Dymond.<sup>1</sup>

The ketoximes are very similar to the aldoximes; but in these bodies, the isomeric forms resemble each other more closely than is the case with the aldoximes, on account of the greater similarity of the groups connected with the carbon. These isomeric forms are also distinguished as *syn* and *anti*, according to the following formulas:—

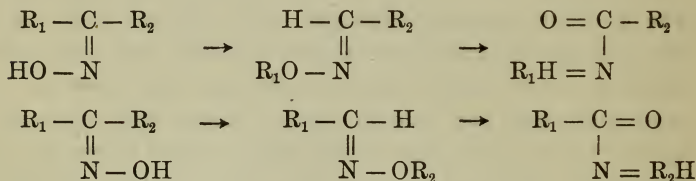


*Syn* phenyl tolyl ketoxime.

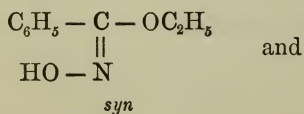


*Anti* phenyl tolyl ketoxime.

For distinguishing between these, the Beckmann reaction is made use of; viz., the transformation of the oxime into the structurally isomeric acidamide. These reactions are indicated in the following formulas:—



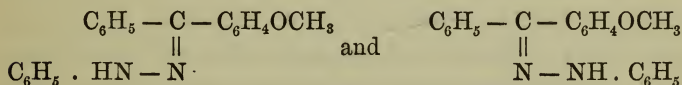
Illustrations of *syn* and *anti* derivatives of hydroxamic acids may be found in the ethyl benzhydroxamic acids,



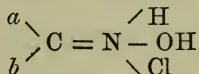
<sup>1</sup> J. Ch. S. 65, 206.

In the case of the dioximes, three isomeric forms are possible according to Hantzsch's formulas, and this number agrees exactly with the number of benzil dioximes which have been discovered. The formulas for these three dioximes have already been given, (p. 123), and, adopting the nomenclature of the other oximes, the  $\beta$  form is the *syn* dioxime,  $\gamma$  would be designated as *anti*, and  $\alpha$  as *amphi*.

An isomerism in the hydrazones, apparently not due to structural differences, was first observed by Fehrlin<sup>1</sup> and Krause<sup>2</sup> in phenyl-hydrazone of *o* nitrophenyl glyoxalic acid. Since then, several other similar cases have been described. These are explained by Hantzsch<sup>3</sup> on exactly the same principle as the oximes, the formulas for the two phenyl-hydrazones of anisyl-phenyl-ketone being written



These are all cases of compounds in which nitrogen with a valence of III is joined by double bonds to carbon. That the same kind of isomerism may be observed when pentad nitrogen is doubly linked to carbon may be inferred from the apparent retention of this isomerism in some salts of the oximes,

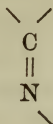


but these bodies have not as yet received a very thorough study.

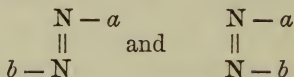
There remains to be considered only the compounds embraced under II. *b*, those in which two atoms of triad nitrogen

<sup>1</sup> Ber. 23, 1574.<sup>2</sup> Ber. 23, 3617.<sup>3</sup> Ber. 26, 9.

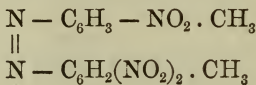
are doubly linked to one another. It is quite conceivable that there may be a stereo-isomerism in these bodies, analogous to that observed in bodies of the type



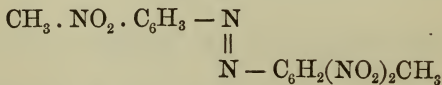
and represented by the formulas



Well-authenticated illustrations of such an isomerism, however, have been lacking until quite recently, and it has been considered doubtful whether such an isomerism did not in reality exist, or whether the lack of the observed phenomenon was to be attributed simply to the fact that bodies of this type have in general a rather complicated structure, and have not been very thoroughly investigated. It has been suggested, however, that this theory may serve to explain the two tri-nitro-azo-toluenes which, according to Janovski, have the same structure:—



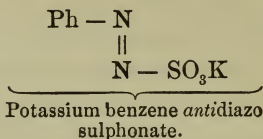
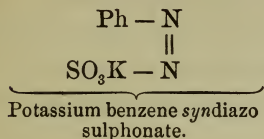
and



Within the present year (1894), Hantzsch<sup>1</sup> has described some stereo-isomeric diazo and diazo amido bodies which seem

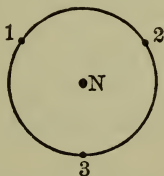
<sup>1</sup> Ber. 27, 1702, 1726-1857.

to belong in the class under consideration. As one illustration, may be mentioned the diazo sulphonates which he represents by the following formulas:—



Several other bodies of this type have been shown by him to exhibit the same kind of isomerism, so that it seems probable that two doubly linked nitrogen atoms may assume configurations in space closely analogous to those exhibited by two doubly linked carbon atoms.

Independently of any conception as to the geometrical form of the nitrogen atom itself, the simplest and most natural assumption as to the arrangement of a molecule containing triad nitrogen is that the nitrogen atom is situated in the centre, with the three combining atoms or radicals arranged around it symmetrically in a plane, and this assumption is in accordance with the facts that triad nitrogen compounds are characterized by stability and an absence of isomerism.



If, however, the nitrogen atom be joined to the carbon tetrahedron by 1 and 2, it is quite conceivable that 3 should be drawn from the plane of the paper by its attraction for one



or the other of the two radicals attached to the carbon, according to Hantzsch and Werner's theory, giving a result similar to what would have been the case if the N occupied one angle of a tetrahedron, and 1, 2, and 3 the other three angles.

When the two dormant valencies of nitrogen are called into play, the problem becomes more complicated, but the simplest assumption is that these two are symmetrically arranged with reference to the other three.<sup>1</sup>



This would make 4 and 5, one below and the other above the plane of the paper. Professor Pickering calls attention to the fact that the law of symmetry would be satisfied if 4 and 5 were the only valence-places saturated. With monad elements, this would probably never occur, since they would naturally take places 1, 2, and 3; but with a bivalent element, it would be quite conceivable that 4 and 5 should alone be saturated, and thus we get a plausible explanation of such bodies as NO.

The above formula is plainly not perfectly symmetrical, which agrees with the fact that there is a tendency for two atoms or radicals to split off and leave the more symmetrical triad nitrogen.

Objections have been urged against the explanation of optical activity, in the completely asymmetric nitrogen molecule, by the assumption that  $(\text{NH})^{\text{IV}}$  may take the place of  $\text{C}^{\text{IV}}$  in a

<sup>1</sup> See Professor Pickering. J. Chem. Soc., Sept., 1893.

tetrahedron, but, adopting the above formula, it will be seen that something entirely analogous to this is possible. If the nitrogen is supposed to occupy the centre of the molecule, and 3 be a hydrogen atom, and 1, 2, 4, and 5 be replaced by four different radicals, then lines joining the last four points would give the figure of an irregular tetrahedron entirely analogous to the asymmetric carbon tetrahedron.

It will be observed that the figure just discussed is practically the same as that of Burch and Marsh.

## V.

### VARIATIONS IN OPTICAL ACTIVITY AND RELATIONS OF STEREO-CHEMISTRY TO CRYSTALLOGRAPHY.

THOUGH there is much in connection with the subject of stereo-chemistry which is still in a vague and unsettled state, though there are many unanswered questions, and so much new matter constantly being brought forward to be sifted and explained that we must feel that our knowledge of this branch is still quite in its infancy, yet it has already done much for the parent science of Chemistry. If in no other way, it has done great service in introducing symbols and formulas which explain better the observed properties of organic bodies than any which have previously been used. It has also stimulated research, and carefulness and delicacy of work in the preparation of many new organic compounds, in improved methods of preparing and purifying bodies long known, and in a more careful study of certain of their properties. This is especially noticeable in connection with the subject of optical activity. It has already been mentioned that when van't Hoff's theory was first announced, various bodies were cited as showing optical activity without asymmetric carbon. To settle this point it was of course essential that the substances should be in a state of absolute purity, and their optical activity determined with the greatest care, thus

leading to much careful experimentation before van't Hoff's hypothesis could be verified.

By the study of stereo-chemistry, the subject of optical activity has gained a new importance and interest on account of the analogy in structure thus suggested between certain crystalline forms and some organic molecules. Since it is found that the rotatory polarization exhibited by quartz and other crystalline bodies is also shown in the solutions of certain organic compounds, we have an indication that these organic molecules are structures whose atoms have a definite and fixed arrangement analogous to the arrangement of the molecules in the crystals. Any new facts, therefore, in regard to the optical activity of organic liquids are to be welcomed in the hope that they may ultimately throw more light upon molecular structure. Communications on this subject are constantly being published in the various scientific journals, some of them relating to the optical activity of particular bodies, others of a more general nature, and the subject is of sufficient importance to warrant a brief allusion here to some of the most recent investigations in this field.

Some of the most important of these investigations have been in regard to the variations which optical activity undergoes under different conditions as to solvent, temperature, etc. That each substance has its own characteristic amount of rotatory power is true if the conditions remain fixed, but the amount varies very much under varying circumstances. It is well known, for example, that the amount of deviation increases proportionally with the length of the column of liquid examined.

As early as 1838, Biot had observed in a few cases that, with solutions of the same concentration of a particular substance, the amount of rotatory power varied with the solvent

employed. These observations were for some time overlooked, but in 1873, A. C. Oudemans undertook some experiments to determine the effect of different solvents on the rotatory power of organic bodies, and found that although some bodies, as sugar, for example, did not alter essentially with the various solvents, others, especially the alkaloids and their salts, suffer considerable deviations.

In 1893 Freundler<sup>1</sup> undertook some experiments to determine the influence of various organic solvents on the rotatory power of certain ethers of tartaric acid. Referring here only to the two solvents tried which gave the greatest deviation from each other, his results are as follows : —

	Solvent.		Solvent.	
With diacetyl tartrate	Carbon disulphide	+36.7°	Bromoform	−2.6°
“ dipropionyl tartrate	“ “	+35.5°	“	−2.0°
“ dibutyl tartrate	“ “	+28.8°	“	−3.8°
“ di <i>n</i> valeryl tartrate	Acetone . . .	+ 8.2°	“	−4.7°
“ di <i>n</i> caproyl tartrate	Methyl alcohol .	+ 5.4°	Benzene .	−2.5°

Freundler found, in general, that oxygenated solvents made little or no change in the amount of rotatory power, while the halogen compounds lower it much, even to changing of sign, as shown in the above results. If the optical activity is to be ascribed, as has been supposed, to molecular structure, it is evident that different solvents, none of which exert any action on the molecule, should not alter the activity of the substance. It has been suggested, however, that the variations in these cases may be due either to polymerization or to combination of the solvent with the active body. Freundler concludes, as

<sup>1</sup> Compt. rend. 117, 556.



the result of his researches, that normal values of deviation are obtained if the molecular weight remains unchanged, and that abnormal values are obtained only with solvents which act upon the dissolved ethers; therefore, his investigations really cast no doubt upon the constancy of the property in an unaltered active compound.

That the amount of rotatory power of an active substance is dependent on the *temperature* is a fact which has long been known, but it is only recently that this variation has been systematically studied. In Landolt's monograph, "*Das optische Drehungsvermögen organischer Substanzen*," published in 1879, it is stated that, so far as then known, increase in temperature is generally associated with diminution of rotatory power. Landolt himself found, however, that the rotatory power of nicotine increases slightly with the temperature; the same has been found true in regard to certain ethereal salts of tartaric acids; and Frankland and MacGregor<sup>1</sup> have observed the same with some glycerates and diacetyl glycerates, so that there seems to be at present no general rule in regard to this variation. The paper of Frankland and MacGregor, just cited, closes as follows: "The results of our experiments as well as those of others clearly show that the effect of temperature on optical activity will have to be more taken into consideration in the future than it has been in the past, and when systematically studied for a large number of active substances, it may assist in throwing light on the internal arrangement of the molecules of active compounds, for it has already been ascertained in several cases that the influence of temperature on rotation is independent of any molecular polymerization."

The possibility of change of temperature producing poly-

<sup>1</sup> J. Ch. Soc. 66, 760.



meric changes, and thus causing optical variations, has been occasionally brought forward as an answer to those who urged that these variations in rotatory power with the temperature were an argument against this power depending in any way upon space relations. To give a concrete illustration, Colson,<sup>1</sup> in 1893, undertook some experiments with active bodies under varying conditions of temperature. The following are the results obtained with the oxide of iso-butyl-iso-amyl, in a tube 0.20 m. long, and the deviations observed with reference to ray D: —

Temperature.	Angle of deviation.
—40°	—0° 6'
—21°	—0° 4'
— 4°	+0° 11'
+15°	+0° 13'
+40°	+0° 15'

It will be observed that in passing from — 40° to + 40°, the angle of deviation has varied by 21', changing sign between — 21° and — 40°. Colson uses these observations as an argument against the theory that the rotatory power depends in any way upon space relations, arguing that if the deviation were caused by the position in space, the rotatory power should not be influenced by physical causes incapable of changing the nature and state of the body; by cooling a body without freezing it, for example, this should remain constant. He therefore concludes that the chemical constitution cannot be the factor preponderating in the value or in the sign of the rotatory power.

As an answer to this, it was urged that changes of temperature may make changes of the nature of polymerization in the aggregate which constitutes the optical molecule, and thus

<sup>1</sup> Compt. rend. 116, 319.

cause these variations. Ramsay has, however, found that some substances whose rotatory power does not vary with the temperature do polymerize, and that others, whose rotatory power is variable, do *not* polymerize. It would seem, then, that the variations must be due to internal changes in the molecule. Le Bel<sup>1</sup> states that all the compounds actually known to have variable rotatory power are simple ethers; i.e., compounds in which the asymmetric carbon is united only with a single radical containing an atom of oxygen attached to another radical. When the asymmetric carbon is united with two radicals of similar constitution, the variations of rotatory power become almost *nil*, indicating that two radicals of the same nature compensate for each other. Le Bel thinks these facts can be explained only on the assumption that the univalent unions become immobile at low temperatures, the molecule undergoing a kind of internal congelation, but they become mobile again at higher temperatures, where, indeed, it is observed that the rotatory power tends to become constant, which seems to indicate that perfect mobility might then be attained.

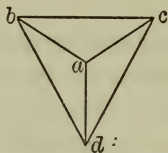
All this study of optical activity shows that it is a property which is very easily influenced by external conditions, but exactly how or why these conditions affect it are points which are not yet very satisfactorily explained. The most that can be said at present is that there is nothing in these variations to cast any serious doubts upon the fundamental principles of stereo-chemistry.

Fock<sup>2</sup> has published some interesting speculations in regard to the *cause* of optical activity, accepting van't Hoff's tetrahedral theory as his starting-point. He recalls the fact that the rotation of the plane of polarization consists in the divi-

<sup>1</sup> Compt. rend. 118, 916.

<sup>2</sup> Ber. 24, 101.

sion of the entering ray of plane polarized light, in the active medium, into two circular rays, vibrating in opposite directions and with different velocities, which, on leaving the substance, are again compounded into one linearly polarized ray. Fleischl has discovered for liquids that in the active substances there is also a true double refraction. Another characteristic of these optically active substances is that when they crystallize, they always crystallize in hemihedral forms, and this, in the generally accepted theories of crystallographers, means that a polarity must be ascribed to the molecules of the hemihedrally crystallized substance. These facts, in the opinion of Fock, are held together and explained by taking as axis of polarity the rotation axis of the molecule, which is determined by a straight line passing through the centre of gravity of the molecule, and that tetrahedral angle to which is attached the radical of greatest mass. In the accompanying cut, if  $a$  is the radical of greatest mass, and if  $b > c > d$ , then this molecule will find less resistance of the ether rotating in that direction than in the reverse.



This would seem to offer a possible explanation of the different velocities of the two circularly polarized rays in opposite directions. He concludes that a rotatory motion of the molecule only produces a rotation of the plane of polarization under the following conditions:—

1. The polarity of the molecule must be exhibited in such a way that a ray of light will find a greater resistance moving in one direction around the rotatory axis than in the other.

2. The rotation of the molecule must take place either to the right or left around this axis.

These two conditions can be met with only in molecules built up around asymmetric carbon.<sup>1</sup>

One of the most interesting ways in which stereo-chemistry is *suggestive*, without offering any definite enlightenment, is in indicating relations between molecular and crystalline structure. It has already been pointed out that the idea of enantiomorphous forms in the invisible molecules is derived from the hemihedral, enantiomorphous forms seen in crystals, and this because the crystals with spiral arrangement of hemihedral faces share the property of rotatory polarization with molecules possessing no plane of symmetry, and which may be considered as built up around asymmetric carbon with a spiral, or circular, arrangement of the atoms either to the left or right. The representation of molecules by regular geometrical forms in three-dimension space, which stereo-chemistry has introduced, cannot fail to suggest at once the thought of a crystal, and to lead to the hope that by a more thorough and systematic investigation of the forms of molecules, it may be possible to trace some connection between these forms and those of the corresponding crystallized substances.

The laws which determine the crystalline form which each particular substance shall assume are as yet beyond our grasp; but there are many facts to show that this is influenced by the complexity of the molecule, and also that each individual atom plays its part in some way in determining the shape of the crystal. Thus it has been shown that a large proportion of the elements and simple inorganic compounds crystallize in the regular and hexagonal systems, while complex inorganic and organic compounds crystallize more frequently in

<sup>1</sup> For Ostwald's criticism of this work, see *Zeit. f. pr. Chem.* 7, 429.



rhombic and monoclinic systems. This indicates a connection between simplicity of molecular form and the largest possible amount of regularity or symmetry in crystalline structure.

The fact that each constituent atom of the molecule may also affect the crystalline symmetry of the body has been shown by Groth and others, who have studied the effect of the substitution of different elements in the molecule of benzene derivatives, and have shown that such substitution is always accompanied by a definite change in the crystalline form. Thus, the substitution of hydrogen by OH or NO<sub>2</sub> leads to changes in the relations of the axes to one another, but not to a change of crystallographic system; but the substitution of hydrogen by chlorine or bromine changes the system to one less symmetrical. This last observation is hardly what might have been expected, since the substitution of one element by another would not increase the complexity of the molecule, unless indeed this may be taken as another indication of the compound nature of the halogen elements.

It would seem as if the facts of isomorphism might be expected to throw more light on the connection between molecular and crystalline structure than is found to be the case. One atom may be replaced by another atom or group of atoms, having the same valence as itself, without changing the crystalline form of the compound, but, on the other hand, another atom of the same valence may, on its substitution, completely change the form of the crystal. There are two ways in which this latter observation may be explained. Either the new atom gives a new shape to the molecule, or it influences the number of simple molecules which go to make up the crystalline unit; and since the valence remains the same, the former

explanation seems at first sight a more natural one than the latter. This would lead to the idea of the crystalline form as depending very closely on the shape of the simple molecules of which it is composed, and it was on an assumption of this kind that Le Bel based his objection to the tetrahedral symbol of carbon.

The difference between the point of view of Le Bel and that of van't Hoff has already been briefly alluded to. In 1890, Le Bel<sup>1</sup> again called attention to these differences, and stated his objections to the tetrahedral idea. He assumes that if  $\text{CR}_4$  has necessarily the geometrical form of a regular tetrahedron, then it follows that all bodies of that general formula should crystallize in the cubic system, and that  $\text{C(R)}_3\text{R}$ , should be rhombohedral. These conclusions he does not find verified by facts.  $\text{CBr}_4$ , for example, he finds does not crystallize in the regular system, and there are other similar discrepancies, from which he concludes that  $\text{CR}_4$  need not always have the form of a regular tetrahedron, but that two forms are possible for a molecule of this type. These two forms he derives by reference to repulsive spheres around the atoms, the arrangement of these spheres depending on the chemical nature of the radical R.

The study of vapors has shown that the attraction of molecules ceases when they approach very near each other, and gives place to a kind of repulsion, as if the molecule were surrounded by a sphere, within which active repulsions exist. Now it is very probable that inside the molecule there are analogous repulsions between the atoms, and that such repulsive forces play a certain part in the equilibrium of the molecule. In the case of an atom confined in a molecule, the oscillations probably do not take place with equal ease in all

<sup>1</sup> Bull. Soc. Chim. [3], 3, 788.



directions, and therefore the repulsive zone will not be a perfect sphere, but the same general reasoning can be applied as if it had a spherical form, and therefore the term "repulsive sphere" is retained.

Applying these ideas to the formula  $CR_4$ , and considering first only the relations between C and R, each of the radicals will be drawn toward the carbon till its repulsive sphere touches that of the latter, when there is developed enough repulsive force to bring them to equilibrium, on the condition that the reciprocal action between the radicals does not oppose this. With the radicals themselves, on the same principle, any two of them may approach each other until their repulsive spheres touch, and this gives the regular tetrahedron as the limit of this system of equilibrium. It is, however, possible that the action of the carbon may predominate over the reciprocal action of the radicals, causing their repulsive spheres to interpenetrate to a certain extent, and this gives another possibility of equilibrium in a second geometrical form.

Le Bel has thus accounted for the possible existence of two different geometrical forms for the molecule  $CR_4$ , and therefore, on the assumption that the crystalline form must possess the same type of symmetry as the simple chemical molecule, he has also accounted for the fact that bodies of the type  $CR_4$  may crystallize in two different systems; but we cannot refrain from asking if such an explanation was absolutely necessary. Assuming that the carbon atom occupies the centre of a sphere, and that its four attendant radicals oscillate about mean positions which bear to one another the relations of the four angles of a tetrahedron inscribed in this sphere, does it necessarily follow that the accumulation of such molecules under the influence of the crystallizing force must arrange

themselves in some form of the regular system? Though this seems at first glance a natural outcome of the assumption, it must be granted that the particular shape of the *crystalline molecule* must depend on the number, no less than the form, of the simple molecules which go to make it up, and can be conceived as belonging to a different type of symmetry from that of the simple molecule. How else can the phenomenon of dimorphism be explained? To explain the existence of orthorhombic and rhombohedral calcium carbonate, one must either assume that the simple molecule  $\text{CaCO}_3$  may have different forms under different circumstances, or that the number of these molecules in the crystalline unit may vary; and the latter seems the more plausible explanation of the two. If this can explain the existence of  $\text{CaCO}_3$  in two crystalline forms, why is it not sufficient to explain the fact that  $\text{CR}_4$  does not always crystallize in the same system?

Certain points in regard to isomorphism indicate that the crystalline form cannot be considered as a direct result of some inherent property of the constituent atoms, such as their form. Manganese, for example, may be isomorphous with chlorine, sulphur, aluminum, or copper, according to the function which it has in the particular molecule, and yet the form of the manganese atom is generally assumed to be unalterable. When, therefore, two elements which are usually isomorphous are found in corresponding compounds which do not exhibit isomorphism, as, for example, the nitrates of sodium and potassium, it is most probable that the configurations of the simple molecules, as  $\text{KNO}_3$  and  $\text{NaNO}_3$ , must be the same, and the difference in crystalline form must then be attributed to some outside cause, as, for example, to the number and arrangement of the simple molecules constituting the crystalline unit.

Recently an attempt has been made by Fock<sup>1</sup> to trace some connection between the tetrahedral form of the carbon atom, and the crystallographic form of certain compounds containing carbon. He considers one of the positive results of stereochemical investigation to be that the affinities of the atoms have not only a definite value, but also a definite *direction*, and this suggests a correlation between the affinity directions of the atoms and the different directions in the crystal in which different properties are observed. The most simple and natural correlation here conceivable is that the crystalline molecule and the crystal itself should possess the same type of symmetry, but it is generally conceded that the crystalline molecule is a larger unit than the chemical molecule, and its exact size is unknown. However, Fock proceeds to show that the explanation of the crystalline form from the chemical composition is not impossible, though until further investigation gives some clew to the actual number of atoms in the crystalline molecule, his paper must be considered as pointing out a pathway to research rather than as leading to any very definite results.

He pictures the carbon atom as a bullet, from which four rods extend to the solid angles of a tetrahedron. Carbon, when crystallized in the form of diamond, shows exactly the type of symmetry exhibited by this carbon atom. In the form of graphite, it crystallizes in the hexagonal system and apparently shows rhombohedral hemihedrism. Now if two carbon atoms are so arranged that two valencies, or *rods*, one from each atom, fall in the same straight line, and the three remaining rods from each of the two atoms, instead of being directly opposite one another, are arranged alternately, as in the figure,

<sup>1</sup> Zeit. f. Krystallographie, xx., 76, 435.



we have the symmetry of the rhombohedral hemihedrism of the hexagonal system. This desired condition of affairs is brought about by the assumption that the crystalline molecule in graphite consists of two carbon atoms, — an unproved and, as Fock himself states, an improbable assumption, but with a larger number of atoms it would not be difficult to construct the symmetry of the hexagonal system in a similar way. On a similar basis Fock attempts to explain the crystalline form of calcite on the assumption that the crystalline molecule is  $\text{Ca}_2(\text{CO}_3)_2$ , and to show some reasons for the similarity in crystalline form of  $\text{CaCO}_3$  and  $\text{NaNO}_3$ .

In other compounds of carbon also, a possible correlation between the crystalline form and the geometrical form of the chemical molecule is shown, but the paper is interesting, not so much for the actual results achieved, as being one of the pioneer efforts to link together stereo-chemistry and crystallography. No one can study the former subject without feeling that it may be destined to give much aid to the latter. Already the analogy in behavior between crystals and organic molecules in regard to polarized light has led to the assumption of geometrical molecules, — the first step in stereo-chemistry, — and now the effort has been started to explain the building up of crystals from these geometrical molecules. If the crystal units of a number of different substances could be determined, the subject would be much simplified, and the bearings of isomorphism and dimorphism might then be discussed more intelligently.

It must be granted that although there are certain relations between stereo-chemistry and crystallography which naturally suggest themselves, they can be but vaguely traced at present, but they give promise of becoming plainer in the future, and thus furnishing another proof of the interdependence of all science; and there seems every reason to hope that many other interesting developments may be brought out by a further study of these two sciences in their relations to each other.



## VI.

### DEDUCTIONS AND SPECULATIONS CONCERNING THE NATURE OF ATOMS AND VALENCE, WHICH HAVE GROWN OUT OF THE STUDY OF STEREO-CHEMISTRY.

THE study of geometrical isomerism cannot fail to stimulate a new interest in the old unanswered questions as to the nature and form of an atom, and the real significance or nature of that property of the atom which we call valence, and the present work would be incomplete without some review and discussion of the various ideas and hypotheses which have grown out of stereo-chemical studies. Stereo-chemistry has given us a much more definite idea of organic molecules than we have ever had before; it has entered so far into their constitution as to represent, in addition to the atomic linking, the relative arrangement of the atoms in space, and also to describe certain definite motions which may be taking place within the molecule; therefore we have some right to suppose that it may be able to throw new light on the subjects of atoms and valence. There are many questions which have long puzzled the most profound thinkers, and it has almost seemed as if they must forever remain unanswered, from the nature of the case, but now that stereo-chemistry has penetrated so deeply into the invisible realm of the infinitesimally small, we begin to ask if it may not go still farther and throw some light on these old hard questions.



In what follows we shall accept the generally received results of stereo-chemistry, and simply ask what conclusions can be drawn from them in regard to atoms and valence. Stereo-chemistry has explained so many cases of isomerism, and is in harmony with so many known facts in organic chemistry, that it can no longer be regarded as a doubtful hypothesis; whatever changes in form or symbolism it may undergo in the future, we cannot but feel that it has sufficient underlying truth, so that its bearings on the subject of the unseen atoms are worthy of serious attention. On many of the questions which have long puzzled us, stereo-chemistry is silent, to a few it gives apparently definite answers, and in regard to others it offers suggestions which may, unfortunately, be variously interpreted.

Some of the questions which have long furnished interesting subjects for discussion are the following: Are the chemical atoms really *ἄτομοι* in the sense of being from their nature indivisible, or are they simply the limit reached by chemical means, just as by mechanical means a tiny fragment may be obtained which we can no further subdivide, though itself made up of parts and therefore conceivably capable of still further subdivision? Are the atoms of the different elements to be considered as so many separate and distinct forms of matter, or should they rather be regarded as made up from one primordial element, differing from one another either in the amount of condensation of the matter, or in the kinds of motion with which they are impressed, or differing simultaneously in both ways? Shall we look upon the atoms of all elements as material points from which forces proceed, and therefore disregard shape and size, or shall we consider them as structures having a finite expansion in space, and therefore capable of existing in different geometrical forms?

Along with these questions must also go queries concerning the nature of valence. Is it an inherent property of the atom, or is it first called into existence by the approach of other atoms? Has it definite location in the atom, is it exerted in certain definite directions, is it to be considered as originally divided into parts in the atom; or is it more of the nature of other attractive forces, an undivided whole, until the near approach of other atoms causes it to be divided among them? In what does the difference of valence in different elements consist? Does it correspond to the difference in different magnets, a difference in the amount of attractive force; or to a difference in the motions of the atoms, perhaps a different number of vibrations in a unit of time; or to a difference in the number of certain particular parts of the atom which we may call valence-places? What do we mean by double and triple linking between two carbon atoms, and what conceptions of valence can explain the fact that doubly linked carbon atoms are not held together with twice the strength of two singly linked atoms, and triply linked with three times that strength?

In taking up this portion of the subject, it cannot be developed from a historical standpoint, since there has been no gradual growth from one theory to another until one is finally left in triumphant possession of the field. We can only take a brief review of some of the most important deductions and speculations which have grown up out of stereo-chemical theories, and discuss and classify them as far as possible.

The three attributes of the atom which enter most into stereo-chemical discussion are its motions, its valence, and its form; and these will be considered, as far as may be, in the order here given, though it is manifestly impossible to separate the three subjects entirely from one another. The illus-

trations and applications of the theories must necessarily be limited almost entirely to the carbon atom, though some generalizations can be drawn which will apply to all atoms.

The most intimate study of molecules has been thus far almost entirely restricted to the investigation of the *relative positions* of the atoms; and although motion is assumed, both of the molecule as a whole and of the component atoms, no very definite hypotheses as to the latter motions have been presented. It is very probable that the next advances will be made in this direction. The rapid advances in physics, in connection with the knowledge of molecular motions, has led to the belief that we can get no satisfactory and adequate idea of chemical phenomena until some account is made of atomic motions, as well as of atomic arrangements. More than once already has attention been called to the necessity of advance in this direction; and though the task seems difficult, to one who has followed the progress made in our knowledge of the internal constitution of molecules during the last twenty years, nothing seems impossible.

Berthelot,<sup>1</sup> as early as 1875, stated it as his opinion that any explanation of the different kinds of optical bodies, based on the arrangement of the atoms in the molecule, was insufficient, but that it was necessary also to take into account their vibratory and rotatory motions. Thus, he suggests that optically active and inactive bodies may be explained in the following way: In a molecular system we may conceive that the atoms all vibrate in the same plane, giving the inactive body; or they may vibrate in another plane, inclined symmetrically to the right or left, in relation to the fundamental atoms, thus giving the right and left bodies; or we may conceive, again, two symmetrical systems touching one another in

<sup>1</sup> Bull. Soc. Chim. [2] 23, 338.

such a way as to give a mean state of movement analogous to that of the inactive body, and this is the neutral body.

Quite recently Molinari<sup>1</sup> has again opened up the subject of vibratory motions in an article under the title, "Stereo-chemistry, or Moto-chemistry?" He offers some objections to the present stereo-chemical theories, strenuously opposes the hypothesis of limited rotation proposed by Auwers and Meyer, and objects to the supposition that rotation must be stopped in doubly linked carbon compounds. In regard to his first objection, — since the idea of limited rotation can hardly be said to rank as a fully developed stereo-chemical theory, having only a very few facts, and those somewhat uncertain, which its most earnest advocates can bring forward in proof of its necessity, — it would seem that it should hardly be used as an argument against the main stereo-chemical theories.

Molinari also argues that unless a bond is something hard and stiff, which does not appear probable, he cannot understand why there should be motion when two atoms are joined with one such bond, and an unnatural state of rest, such as is met nowhere else in the universe, when the two atoms are doubly linked. But van't Hoff's hypothesis does not state that all motion is necessarily stopped in such compounds, — only that one particular kind of motion must cease. Rotation around the axis joining the two carbon atoms is now impossible, but oscillations to and fro around a fixed mean position may still take place.

An objection against the stereo-chemistry of to-day, however, which cannot be gainsaid, is that there are still a number of facts of organic chemistry which cannot be explained by our present theories. The facts of tautomerism, for example, show that any theory with relation to the position of the

<sup>1</sup> J. f. pr. Chem. 48, 113.



atoms is insufficient to explain *all* phenomena; and it would seem that a theory of motion must be introduced to account for such bodies. Molinari also mentions several instances of isomerism still unexplained, — some of these, however, being rather doubtful cases, and asks if the different isomeric forms could not be equally well explained by the supposition of differences in the motions of the atoms. His ideas are interesting, partly because suggesting a dynamical basis for valence; but it is certainly questionable whether any theory of motion, taken by itself, would prove any more satisfactory than a theory of position alone. It is probable that before every possible case of isomerism is explained, both the arrangement and motions of the atoms will have to be taken into account.

To illustrate, briefly, Molinari's theory, since the valence of carbon is IV, we may assume that it makes four vibrations in one unit of time. In

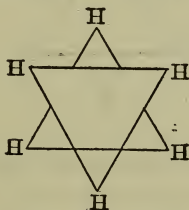


C may either strike *a* once, then *a'*, then *b* and *b'*, and repeat this motion periodically; or it may strike *a* first, then *b*, then *a'* and *b'*; and if *a* and *a'*, and *b* and *b'*, represent the same elements, these are the only two kinds of impacts possible. The question might here be raised, if isomerism depends on the kind of impacts, — and there may be two such impacts for a body like  $\text{CH}_2\text{Cl}_2$ , — why may not that body exist in two different isomeric forms?

According to Molinari, double linking between two carbon atoms might indicate two consecutive and inseparable impacts in unit of time. The theory is ingeniously worked out for

benzole and other compounds, but need not be discussed in detail here, since it is a practical abandonment of stereo-chemistry for a much less complete and satisfactory explanation of the facts observed. In connection with these studies it is only interesting to note that the deeper investigation of the molecules undertaken in stereo-chemistry has led to the stronger feeling that the motions of the atoms are also of the greatest importance.

A portion of Bischoff's work has already been briefly alluded to, but his "dynamic hypothesis" may appropriately be taken into consideration here as indicating the tendency to take the *motions* of the atoms into account in explaining chemical phenomena. It will be remembered that he thinks the position of stable equilibrium is best represented by assuming that the radicals attached to two singly linked carbon atoms are as far apart as possible. Thus, the molecule of ethane, viewed from above, would be represented by him as follows:—

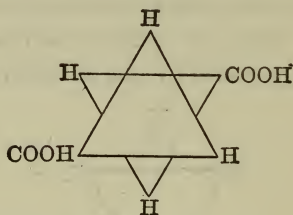


In the above formula, since the three groups attached to one carbon atom are all alike, the figure formed by joining these groups by straight lines is an equilateral triangle; if the groups were  $\text{CH}_3$ ,  $\text{CH}_3$ , and  $\text{COOH}$ , it would be an isosceles triangle; and if  $\text{H}$ ,  $\text{CH}_3$ , and  $\text{COOH}$ , the triangle would be scalene. Whether the planes represented by the two triangles are parallel, or inclined to one another, does not enter into the discussion.



From the dynamical standpoint, that configuration is most favorable for stability in which the individual components of the molecule are reciprocally hindered the least in their oscillations.

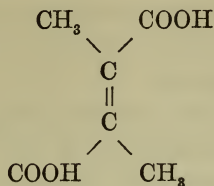
If, in the above formula, two adjacent hydrogen atoms are replaced by carboxyls, the result of raising the temperature will naturally be to increase the oscillations of these atoms, until it may happen that they approach near enough to be within each other's sphere of action, when water splits off. This Bischoff calls a "collision." Now, it has been found that the addition of methyl groups increases the ease of dehydration, and Bischoff explains this by assuming a repulsion between methyl and carboxyl. Succinic acid, according to him, is represented by the formula,



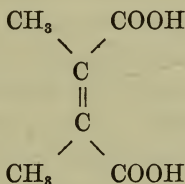
in which the carboxyls keep as far apart as possible, on account of their weak repulsion for each other. By the introduction of methyl for one of the hydrogen atoms, the stronger repulsion between methyl and carboxyl drives the carboxyls as far as possible from the methyl, and therefore nearer each other, making it easier to form the anhydride, as is found in fact to be the case. This ease of dehydration increases as the number of methyl groups increases, tetramethylsuccinic acid forming its anhydride most easily of any.

The repulsion between alkyl and carboxyl groups finds a

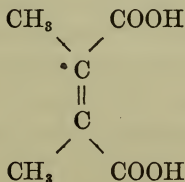
farther support in the non-existence of a methylmaleic acid of formula



which, according to Wislicenus's view, should be stable, whereas all reactions in which the formation of this body might be expected, give, instead, the anhydride of its geometrical isomer, pyrocinchonic acid,



The same is true in regard to ethylmaleic, or xeronic acid. Here the space taken up by the groups in their oscillations seems to be a matter of some consequence. Thus, the superior stability of



over its geometrical isomer is explained by Bischoff on the assumption of repulsion between methyl and carboxyl; but in

this molecule the methyl groups take up so much more room than would be occupied by hydrogen atoms that there is a crowding together of atoms inside the molecule, a limiting of vibrations, so that collisions take place more readily, resulting in the splitting off of water.

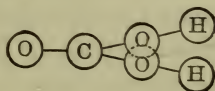
A collision between two carboxyl groups leads to a splitting off of water; when methyl collides with carboxyl, there is no chemical interaction, but the carboxyl is driven back along the path through which it came, and the oscillations are limited in extent. Bischoff<sup>1</sup> thinks that through the limitation of vibrations, caused by introduction of alkyl groups, certain systems which have been considered as freely rotatable around an axis may be so only up to a certain limit, and that, therefore, configurations which have been considered identical are not necessarily so; but configuration symbols may be produced for two bodies, differing in the same way as the ordinary geometrical isomers, though perhaps less in amount. To this new kind of isomerism, based on the consideration of the space filled by the radicals, and the shortening of the distance between the carbon atoms caused by this, he gives the name, "dynamical isomerism." In these bodies the kinetic energy of the individual motions of the atoms inside the molecule is not sufficient to conquer the resistance which the jostling of the radicals against each other opposes to the rotation of the one form into the other. If energy is added, then the impacts may become so lively that this resistance is overcome, and by increasing the distance of the carbon atoms from one another by heat, the transformation of one form into another may be accomplished.

Bischoff has applied his views very successfully to the explanation of the substituted succinic acids,<sup>2</sup> and also to the  $\gamma$

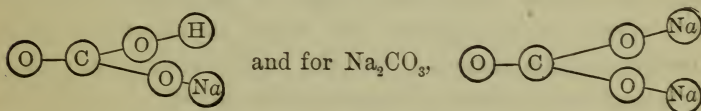
<sup>1</sup> Ber. 23, 623; 24, 1077.

<sup>2</sup> Ber. 24, 1085.

ketone acids;<sup>1</sup> but they do not seem to be in a sufficiently clear and definite form to be of very general application at present. This "dynamical hypothesis" has also been used by Bischoff to explain the stability of certain bodies, such as the carbonates, notwithstanding the instability of the closely related compound, carbonic acid.<sup>2</sup> According to this explanation, the sodium, for example, will not take the exact place of the hydrogen atom, for which it is substituted, but on account of its greater attraction for the oxygen it will draw the latter atom nearer to itself, and farther from the carbon. Thus, we may represent carbonic acid by the following formula, in which there is not room for free oscillation, but a collision would occur by which water would be given off: —



If, however, one of the hydrogen atoms be replaced by sodium, the following formula results: —



In these last two formulas, the attraction of sodium for oxygen is shown to have drawn the latter farther from the carbon, and thus the interference seen in carbonic acid is avoided.

Another possibility suggested is that the introduction of the sodium may alter the angle between the carbon and oxygen without changing the distances between the atoms. This possibility is represented by the following formulas: —

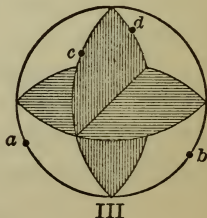
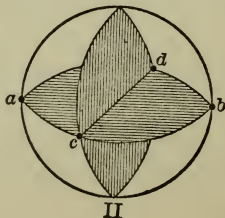
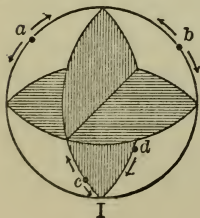
<sup>1</sup> Ber. 26, 1452.

<sup>2</sup> Ber. 23, 3414.



Now, it is possible for two hydroxyl groups to be as near together when joined to two different carbon atoms as when both are united to the same one, therefore exactly similar explanations may be applied to other bodies as, for example, to show why pyrocinchonic acid exists only in the form of the anhydride, whereas its ethyl salt is stable.

Another attempt to explain observed phenomena by reference to the motions of atoms is made by Werner, who refers the change from the active to the inactive body, under the influence of heat, to the oscillations of the atoms in the molecule. His idea of the carbon atom is a sphere with four "valence-places." These valence-places are the four points where lines joining the centre of gravity of the carbon atom with the centres of gravity of each of the four radicals, cut the surface of the sphere. The atoms are assumed to have certain periodic motions around the valence-places, and certain influences can increase or decrease these motions. Among the simplest forms of oscillation, we may assume that the atoms vibrate in two planes at right angles to each other.





In Figure I., suppose  $a, b, c, d$ , to be four radicals oscillating in the directions shown by the arrows. Then, if these motions be increased by heat, the atoms may vibrate so far as to reach the position shown in Figure II. From this position, they can pass as readily into that shown in III. as to return to their original position, therefore the final result of heating such a configuration as that shown in I. would be to produce equal amounts of I. and III. If, then, I. represents an active body, and III. its geometrical isomer, the result of heating either would naturally be to produce inactivity.

The facts in regard to the motions of atoms, as derived from a study of stereo-chemistry, are certainly not very definite. Constant atomic motion of one kind or another is assumed. In the case of singly linked carbon atoms, a revolution of the two atoms in opposite directions around an axis joining the two is supposed possible, but when the kind of linkage changes to double or triple, the rotatory motion is assumed to cease, so that in the resulting molecule the only motions possible are those of the molecule as a whole, an oscillatory motion of the radicals connected with the carbon, and vibratory motions of the carbon atoms themselves. Bischoff adds to this the idea of the oscillations of the atoms in the molecule, producing such jostling against each other that certain groups are shaken off, thus accounting for various decompositions. It is plain that in this he also takes into account the *size* of the atoms, and assumes that they are not inconsiderable in relation to the distance between them.

It is very evident that one of the weakest points in our knowledge of atomic science to-day is in regard to the motions of the atoms, upon which, doubtless, depends the explanation of many phenomena. On the subject of valence, stereo-chemistry leads, perhaps, to more definite notions than in



regard to atomic motions. It is almost impossible to accept all of the stereo-chemical theories without getting the impression of valence as having a directive action; unlike the force of gravitation, for example, the force which draws other atoms to carbon seems to be exerted only in certain directions, or from certain points of the atom. Fock has already been quoted as stating that "One of the positive results of stereo-chemical investigation is to show that valencies have a definite *direction*." Some adopt this view without any further explanation; others attribute it to the existence of four *places* on the carbon atom, which are qualitatively different from the rest of the atom, and which are called valence-places. It is, therefore, plainly impossible to separate the subjects of valence and form of the atom entirely from one another; they must be considered together.

Because many cases of organic isomerism can be best explained by the geometrical conception of a tetrahedron having the carbon atom in the centre, and the combining atoms or radicals in the solid angles, are we to assume that the carbon atom has really this geometrical form, with its attractive force concentrated in the four solid angles, or is this to be taken merely as a useful symbol? And if the latter, what is there in the actual nature of the atom which could correspond to such a symbol? Since van't Hoff has been the leader in the use of this symbol, it becomes interesting to find out what his own ideas were in regard to the nature of the carbon atom. In his earliest work, although he does not express himself definitely on the subject, he tacitly assumes that the atom is a material point. We have no difficulty in reconciling the tetrahedral symbol with this view, so long as we confine ourselves to a single carbon atom. We suppose this material point to be endowed with a certain amount of attractive force, such

that it can hold four hydrogen atoms. These four atoms will naturally arrange themselves regularly around the carbon, and may, therefore, determine the solid angles of a regular tetrahedron. If the four combining atoms are unlike, the general tetrahedral form will still be kept, though it may become irregular, owing to an unequal distribution of the attractive force between the four atoms or radicals, or to the action of these on each other.

In the case of singly linked carbon atoms, the possibility of rotation around an axis must be assumed, and it becomes questionable whether this is reconcilable with the conception of the atom as a material point, since, in the words of Clerk Maxwell, "Even an atom, when we consider it capable of rotation, must consist of many material particles." Even more serious difficulties confront us when we try to reconcile this view with the conceptions of doubly and triply linked atoms. If the atoms are material points, the force holding them together must act directly in a straight line between the two atoms, whether they are singly or doubly linked. Then why should rotation of the atoms in reverse directions be impossible in the latter case? This cessation of rotation would require for its explanation the idea of the attractive forces between these two points acting in two different directions, and cutting each other at an angle, which is manifestly inconceivable.

If we accept van't Hoff's explanation of the isomerism in the ethylenic compounds, we are thus compelled to reject the idea that the carbon atom is a material point, or even a homogeneous sphere, sending out force in all directions. We are apparently forced to the conclusion that there are definite *points* in the atom from which the attraction proceeds, or that for some reason it proceeds only in definite *directions*, or that

it depends in some entirely unknown way upon the kind or rate of motion of certain parts of the atom, supposing it to be made up of parts.

Lossen<sup>1</sup> was one of the first to point out the above-mentioned discrepancy in van't Hoff's work, and stated it as his opinion that atoms are not material *points*, but that parts are to be distinguished, from which the attraction for other atoms proceeds. He criticised the workers in stereo-chemistry in general on the ground that until more was known concerning the shape, size, and nature of atoms, we were not in a position to decide as to their arrangement in space.

This drew forth an answer from Wislicenus,<sup>2</sup> in which is set forth, briefly, his own conceptions of atoms. He urges that the question of atomic *arrangement* in space is capable of experimental proof, and the study of this is the only way he knows of to lead up to the answer of questions concerning the shape and size of atoms. He agrees with Lossen that the results of stereo-chemical investigation exclude the supposition that the atoms are material points, and thinks that what we call an atom is more probably a complex body. Though he states that no positive answer has yet been given by the inferences from stereo-chemistry, he considers it more probable that the atoms are structures occupying space, and made up of atoms of some primordial element, than that they are points bearing energy; that they are, therefore, comparable to compound radicals, and that, like the latter, their units of affinity have position in certain parts of them, from which they work. He considers it not impossible that the carbon atom is a structure which, in its form, approaches more or less nearly to a regular tetrahedron, perhaps very nearly; and that the cause of that force which reaches its outward manifestation in the

<sup>1</sup> Ber. 20, 3306.

<sup>2</sup> Ber. 21, 581.

form of "units of affinity" may be concentrated in the solid angles of the tetrahedral figure, similarly, and on analogous grounds, to the electrical action of an electrically charged metallic tetrahedron.

Since this is applying the results of stereo-chemical investigation to the shape of the carbon atom with the most literal exactness, there can, of course, be no collision between the two.

The old question as to whether that which resists all of our efforts at subdivision, so that we call it an atom, is to be considered a simple unit, from its very nature indivisible or not, is thus answered in the negative by Wislicenus, who considers that it is more probably a structure, and therefore capable of existing in a definite geometrical form. Now, whether an atom is really made up of parts or not, it is certain that it is so constituted, or so endowed with a particular kind of motion, that it resists further subdivision with the greatest tenacity, and this seems more compatible with a spherical shape than with such a form as the tetrahedral. Karsten says that a crystal is the result of cohesion working unequally in different directions; but if the cohesion works equally in an infinite number of directions, the result is a sphere. The idea of the tetrahedral atom suggests this difference of cohesion in different directions, which might be expected to give the atom a tendency to break in certain directions, and therefore destroy its stability. The figure of an atom with sharp corners also suggests to the eye the possible breaking off of these corners; i. e., the subdivision of the atom, on slight provocation.

Another fact which would seem to be opposed to Wislicenus's suggestion, which, it must be remembered, he brought forward only very tentatively, is that, according to this, two



triply linked carbon atoms should present the most stable configuration possible. Two tetrahedrons held tightly together by the forces concentrated at three solid angles of each, no rotation possible, where is there a point of attack? How, then, can the comparative instability of such bodies be explained, and the ease with which addition compounds are formed? In fact, it is difficult, with this conception of an atom, to see how it is possible for a double linkage to be anything but exactly twice as strong as a single, and a triple union to possess three times that strength. This is an objection which has often been brought against "bonds of valence," however used. It is urged that if a "bond" is a unit of attractive force, then a double bond must necessarily have twice the strength of one, etc. Certain conceptions of valence have, however, grown out of stereo-chemical discussions, which show this not to be a necessity, and in so far agree with the results of experience; and some investigators have gone so far as to calculate, from the assumptions made, a mathematical value for the relative strength of single, double, and triple linkage.

The chemists who have given the most attention to the subjects of double and triple bonds, and the change from one form of linkage to another, are von Baeyer and Naumann.

Von Baeyer's strain theory has already been referred to in connection with ring formations. This first appeared in 1885,<sup>1</sup> in connection with his study of the polyacetylene derivatives. He argues that the explosibility of these compounds must depend upon the setting free of heat, and suggests that the energy thus set free may have been held originally in the molecule in the form of a "strain," produced by the bending of the axes of valence from their normal position. He assumes

<sup>1</sup> Ber. 18, 2269.

that the carbon atom is provided with four such axes, extending in the directions of the angles of a tetrahedron as their normal position. In passing from single to double linkage, two of these axes must be bent from their normal position until they are parallel; i. e., each one must be turned through an angle of  $54^{\circ} 44'$ . In passing from single to triple linkage, three axes must be made parallel; i. e., each one turned through an angle of  $70^{\circ} 32'$ . The greater the deviation from the normal position, the greater is the strain, and consequently the less the stability of the resulting body. He points out the correspondence between these ideas and the results of Thomson's thermo-chemical investigations, but also mentions one fact which seems to be out of harmony with his theory. This is that hydrogen easily changes diacetylene carbonic acid to propargylic acid, according to the following equation: —



In this reaction, the single linkage is shown to be attacked before the triple. The weak point of von Baeyer's explanation seems to be the difficulty of conceiving of anything actually existing in the molecule corresponding to such elastic, flexible wires as he pictures in his theory, — the only possible explanation of which has been advanced by Wunderlich, whose work will be reviewed later.

Naumann assumes that the attraction between two carbon atoms comes to its greatest force if the direction of the attraction coincides with the line joining the centres of gravity of the two atoms. If the direction of attraction deviates from the centre-of-gravity line, then the attraction comes into effect only in that component of the force which lies in the above-



named direction. For example, in the case of singly linked atoms, the full attraction comes into force; not so, however, with doubly linked atoms. For, representing the centres of gravity of two carbon atoms, doubly linked, by S and  $S_1$



the attraction, instead of working directly from S to  $S_1$ , is directed from S and  $S_1$  to E and  $E_1$ , and only that component which works in the direction  $S S_1$  can produce any effect, since the other components will be equal and opposite in direction, and therefore neutralize each other.

Starting with these premises, and letting S equal the centre of gravity of the carbon atom considered as tetrahedral, E the angle of the regular tetrahedron, K the middle point of an edge, and F the middle point of a face, it becomes an easy matter to find the relative strengths of single, double, and triple linkage. The full strength of the attractive force, represented by S E, is put equal to 1. In double linkage, as shown in the above figure, only the component S K is taken into account. Knowing S E = 1, by the solution of triangles, S K = .5774, but since there are two such bonds, the full force of the attraction is represented by  $2 \times .5774 = 1.1548$ . Similarly in triple linkage the force of each bond is represented by S F, and this is found to equal .3333, and the total force of the three bonds will be  $3 \times .3333 = 1$ .

From the above results it would follow that the same force must be required to separate two carbon atoms when they are singly as when triply bound, but that a greater force is necessary if they are doubly linked; also, that in passing from triple to double linkage, each bond, still occupied in holding together the carbon atoms, gains an amount of energy which may be represented by the number .2441, and in passing from double to single linkage the gain in energy is considerably greater, being represented by the number .4226; or this may be stated, that it requires a greater force to change from double to single linkage than from triple to double. The reverse changes can take place only in consequence of strong deviation of the atoms from their mean position of equilibrium. By heat, for example, the oscillations of two singly linked carbon atoms may be so increased that they assume double linkage, etc.

Naumann carries his speculations a step further, and says that these same considerations may be applied to other polyvalent elements, if we assume that the distance between the points of attack of two valence units of other polyvalent atoms are equal to those of carbon, and that the centres of gravity of the atoms have positions corresponding as nearly as possible to that of the carbon. Thus he would represent nitrogen, and other triad elements, by an obtuse pyramid, whose base equals one face of a regular tetrahedron; bivalent elements, by an isosceles triangle, whose base is the tetrahedral edge of a carbon atom, and whose height equals the distance from the centre of gravity of the carbon tetrahedron to the middle point of an edge. Interesting as these speculations may be, however, it seems useless to spend much time upon them until more reasons appear for the assumptions upon which they are based.

It is easy to see from these considerations that Naumann's idea of the carbon atom is not that of a material point, but rather of a structure having four parts corresponding to the solid angles of a regular tetrahedron, which differ in properties from the rest of the atom, and may be called valence-places. It does not appear, however, why all of the attractive force of the atom should be directed from the centre of gravity of the atom toward these valence-places.

One of the most valuable and interesting discussions of the carbon atom which has ever been published was made by Dr. Aemilius Wunderlich in 1886.<sup>1</sup> The assumptions which he makes in regard to atoms are as follows:—

(1) The atom is a finite quantity of matter occupying a finite quantity of space.

(2) At any given time the atom must possess a particular form. Since any deep-seated, constantly recurring *change* of form would tend to divide the atom, it cannot be far from the truth to say that the atom has a *fixed form*.

(3) On an atom of valence  $n$ , there are  $n$  "valence-places," characterized by the fact that the atom is satisfied when each of these  $n$  places is separated from a similarly characterized place on another atom of the same, or a different element, by a space which is small in comparison with the size of the atom.

Applying these assumptions more particularly to carbon, on each atom there are four places, or parts, having different properties from the rest of the atom, and these are shown to be equidistant from each other, thus determining the surface of a sphere. Disregarding for the time the shape or size of these valence-places, they are made up of matter, and thus

<sup>1</sup> Configuration Organischer Moleküle. Commissionsverlag von Bruno Leitholdt, Leipzig.

each must have a centre of gravity. A line passing through a centre of gravity of a valence-place, and that of the atom itself, is called an axis; and a plane perpendicular to an axis, and passing through the centre of gravity of a valence-place, is called a valence-plane; and for simplicity and convenience, these valence-planes are generally referred to in describing atomic union, rather than the more vague valence-places. There are four of these planes, and they cut each other in the edges of a regular tetrahedron, called the combination tetrahedron.

Now, two carbon atoms may approach one another in such a way that their valence-planes shall lie parallel to one another, but it will be impossible for them to *touch*, since the whole of the valence-place is conceived as full of matter, and two bodies cannot occupy the same place at the same time. The nearer the valence-planes are to one another, however, the stronger will be the union. It is conceivable that two valence-planes should be near enough together to constitute union, and yet that they should be inclined at an angle to one another instead of being parallel. This state of affairs would correspond to the bending of the wires in ordinary wooden models, and thus is offered a possible explanation of von Baeyer's "strain" theory. As there are three known modes of combination between two carbon atoms, so there are three main positions for two united tetrahedrons.

Here, then, by an entirely different mode of reasoning he has arrived at the idea of forms exactly like those of van't Hoff; but in Wunderlich's conclusions, single linkage is represented by the close approach of two tetrahedral *faces*, and triple linkage is produced by bringing three faces of one tetrahedron simultaneously as near as possible to three faces of the other; i. e., in having one solid angle from each in close



proximity to that of the other. These figures are reversed in Wunderlich's and van't Hoff's schemes, because in one the seat of the valence is placed in the faces, and in the other in the solid angles.

Wunderlich's ideas seem to be in complete accordance with the facts observed in double and triple linkage. In the case of two singly linked carbon atoms, the two combination tetrahedrons have two faces parallel, and very close to one another. To change from this form to double linkage, these tetrahedrons must be rotated until two valence-places come as near together as possible, — that is, until the two tetrahedrons have an edge in common; but now the combination-planes are no longer parallel, but inclined to one another, and so the strength of each unit of affinity is weakened. Similarly, in changing from double to triple linkage, a still further rotation must take place, until three valence-planes of one carbon atom are equally distant from three valence-planes of the other carbon atom, — a state of equilibrium which is reached when the two tetrahedrons have a solid angle in common; and in this case the combination-planes are still farther inclined toward one another, and therefore the strength of each union is still more decreased.

It may be mentioned here that Skraup, adopting Wunderlich's views, has offered an explanation of Wislicenus's theory in regard to the addition products formed from doubly linked carbon compounds. It is to the effect that double linkage, while forbidding rotation, admits of oscillations, such that two valence-places will approach each other, while the other two draw further apart. It is while the two valence-places are furthest apart that the union is most easily broken by the addition of new radicals, and thus it is that the two added radicals occupy "corresponding" positions.

The forms which have been described for singly, doubly, and triply linked carbon atoms have been called, by Wunderlich, the "main positions;" but he also assumes the possibility of union in intermediate positions, — for example, cases of single linkage in which the combination-planes are not exactly parallel, and illustrations of this kind he finds in the ring formations. In penta-methylene, for example, the mutually saturating combination-planes are not quite parallel, and consequently the centres of gravity of the valence-places are not quite so near one another as they are in  $C_2H_6$ . Reckoning the amount of deviation in the  $n$  methylene ring from the formula,

$$\frac{360^\circ - n(70^\circ 31' 44'')}{n}$$

it is seen that the mutually saturating combination-planes from di- to penta-methylene rings are always approaching nearer to one another, but from that point they diverge again.

Wunderlich finds the benzene formula of Kekulé more in accordance with his assumptions than that of Ladenburg, and he has also attempted to apply his theories to other elements than carbon, notably nitrogen and sulphur.

It has been seen that the assumptions which Wunderlich makes, which are of importance in the development of his theory, are that the carbon atom is a body of some size and shape, and that it has four portions equidistant from each other, which are distinguished as the valence-places. If we assume that the actual shape of the atom is that of a tetrahedron, these valence-places are located in the centres of the faces; but the atom may be quite as satisfactorily represented as a homogeneous bullet, from which four equally large segments have been cut away, so that each of the four resulting faces on



the spherical surface has the same position with relation to the other three, and each represents a valence-place.

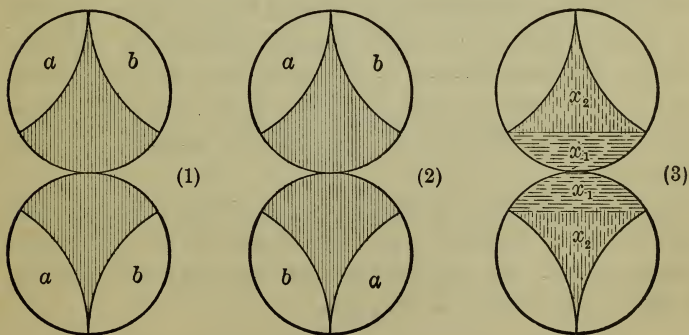
Auwers, accepting Wunderlich's ideas in regard to the valence-places, and assuming that the attraction varies inversely as the square of the distance between the combination-planes concerned, has calculated the ratio of the strength of the double link to that of the triple, and finds it to be 3.56 : 1, if the atoms have the tetrahedral shape. If the atoms are spherical, this ratio becomes 1.65 : 1.<sup>1</sup> His calculations also show that the strength of the double and triple bonds is greater on the assumption of spherical than of tetrahedral atoms, and though they cannot be directly compared with the single linkage, they can never be two and three times as great.

Granting that stereo-chemistry teaches that valence acts as a *located* or *directed* force, there is still room for a difference of opinion as to whether it has this definite location inherently, or whether it is induced by the approach of other atoms; and also as to the general nature of the force or property. In regard to the first question, very little has been definitely stated by most writers on the subject, but it seems to be tacitly assumed that the carbon atom has four *places* or *portions* which are different from the rest of the atom, and in which the attractive force is located. The objection to be urged against this is that it makes the atom a more complicated structure than its practical indivisibility would render probable. If the differentiation in these four particular places is due either to a different kind of matter, or to a different kind of motion, it would appear to have a tendency to destroy the unity of the atom. If due to a different amount of condensation of the same kind of matter as that composing the rest of the atom, it is difficult to conceive of its being inherent,

<sup>1</sup> *Entwicklung der Stereo-chemie*, pp. 28-34.

though it is quite conceivable that this greater condensation might be induced in certain portions on the near approach of other atoms. This would suit perfectly Wunderlich's conception of a sphere with four equidistant segments removed, — the removed segments being replaced in this conception by a more attenuated form of matter; but the difficulty is to reconcile any such idea with the impossibility of free rotation in doubly linked compounds. That one portion of stereo-chemical theory seems to necessitate the conception of the carbon atom as existing with four definite and inherent valence-places.

Nevertheless, Werner<sup>1</sup> does not consider the results of stereo-chemistry incompatible with the idea of valence as an attractive force, working symmetrically from the centre to the surface of the atom, conceived as spherical and homogeneous. On this supposition, the four radicals, combined with the carbon, will lie in the angles of a tetrahedron, because in this position the greatest exchange of affinity between the atoms can take place. According to this, there are no separate valencies, and no real double or triple linkage. The system,  $a b C C a b$ , will be stable in two different configurations, Figs. (1) and (2) : —



<sup>1</sup> Beiträge zur Theorie der Affinität und Valenz.

Two portions of the total amount of attractive power in each carbon atom are used up in holding  $a$  and  $b$ , and two portions are left to hold the other carbon atom. According to Werner,  $x_1$  must be thus used under all circumstances, and does not hinder free rotation; but the portions called  $x_2$  are only used to hold the two carbon atoms together under special circumstances, and therefore these are the portions which hinder the free rotation. This  $x_2$  is small in proportion to the total amount of attractive force, and can be weakened by heat, and in other ways, until it no more opposes the effort of the groups  $a$  and  $b$  to assume the most favorable configuration. Such is Werner's theory; but it is far from being entirely satisfactory, since he does not make it clear in what way this  $x_2$  limits the rotation.

Van't Hoff, in his "Ansichten ueber Organische Chemie,"<sup>1</sup> regards the chemical union of atoms as a consequence of gravitation. If the form of an atom is not spherical, he shows that the amount of attraction of that atom for others will be marked by a certain number of maximum points on the surface of the atom, which maxima depend on the *form* of the atom, and may have different values. The number of these maxima is considered as expressing the valence of the atom. Assuming that the form of the atom changes through its vibratory motions, then the valency of the atom may vary with variations in the state of motion of the atom, and these variations will be conditioned by temperature, nearness to other atoms, etc.

Another suggestion in regard to the nature of valence has been made by Sachse,<sup>2</sup> who has endeavored to explain the phenomenon on the supposition that the atoms are made up of little parts similar to magnets.

<sup>1</sup> Part I. pp. 2-5.

<sup>2</sup> Zeit. ph. Chem., xi., 185.

The idea that the chemical union of atoms is a phenomenon of an *electrical* nature is an old one. Berzelius advanced the idea that two atoms of different elements coming into contact excited each other electrically, like the metals in Volta's experiment; but he supposed that the quantity of electricity collected at the point of union of two atoms depended on their chemical affinity for each other. This Faraday proved to be a mistake, showing that, so far as this electricity came forth in electrolytic decomposition, its quantity did not at all depend on the degree of affinity, but was rather connected with the valence. Thus he found that, using currents of constant intensity in decomposing different compounds, the amount of decomposition in cells containing different electrolytes is exactly proportional to the chemical equivalent of the elements which were either separated or converted into new compounds.

Helmholtz,<sup>1</sup> who, in 1881, directed the attention of chemists anew to Faraday's work, says: "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity is also divided into definite elementary portions which behave like atoms of electricity. The same atom can be charged in different compounds with positive or negative electricity. Faraday believed that the forces termed chemical affinity and electricity are one and the same. I think the facts leave no doubt that the very mightiest among the chemical forces are of electrical origin. The atoms cling to their electric charges, and opposite electric charges cling to each other; but I do not suppose that other molecular forces are excluded working directly from atom to atom."

In the new edition of Watts's "Dictionary of Chemistry,"

<sup>1</sup> J. Chem. Soc. Trans. for 1881.



in the article on Isomerism, Armstrong says: "The deduction from Faraday's law of electrolysis, that definite, as it were atomic, charges of electricity are associated with the atoms of matter . . . is the only approach yet made to a theory of valency; but hitherto chemists have avoided the subject from this point of view."

In 1888, however, Victor Meyer and Riecke<sup>1</sup> published a paper containing an electrical explanation of valence, based partially, at least, on studies in stereo-chemistry. Riecke had approached the subject from the physical standpoint, and, by his studies in pyro-electricity, had come to the conclusion that each valency is caused by a certain combination of two oppositely electrified particles, and Meyer had reached a similar conclusion from his chemical study of the benzil dioximes and other bodies. The latter, from the study of certain cases of isomerism already mentioned, draws the conclusion that in case of single linkage between two carbon atoms, there may be two different kinds of combination,—one in which free rotation in reverse directions is possible, and another in which it is impossible.

As this is as far as the chemical outlook can carry the subject, it is next attacked from the physical side. The facts of frictional and galvanic electricity lead to the assumption that the chemical elements are not simply combined *among each other* by the working of affinity, but that effects of the same character also result between the chemical elements and the electric fluids. The phenomena of pyro-electricity lead to the assumption that the molecules of the pyro-electric crystal are combined with a system of electric poles which possess a fixed position with relation to each other, and to the molecule itself; and it is but a step farther to suppose that the *atoms* may be

<sup>1</sup> Ber. 21, 946.

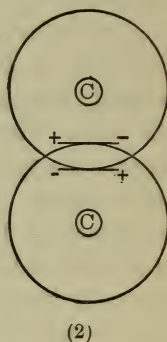
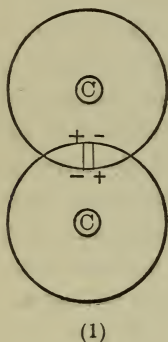
surrounded by similar systems of electrical poles. It has already been pointed out that some deductions in regard to the connection of electricity with atoms may also be made from Faraday's law of definite electrolytic action, which Meyer formulates as follows: "If a current passes for the same length of time through several electrolytes, in each of these the same number of valencies is loosed." This makes a very close connection between atoms and electricity, and especially between the valence of the atom and its electric charge, since the amount of the charge seems to be the same in all atoms of monad elements, double that amount in dyads, etc.

Such considerations as the preceding have led Meyer and Riecke to the following assumptions: The carbon atom is surrounded with an ether envelope, which is spherical, like the atom itself; and its diameter is several times larger than that of the atom. The atom itself is considered as the bearer of the specific affinity, and the surface of the envelope as the seat of the valence. Each valency is conceived as produced by the existence of two oppositely electrified poles, represented as situated at the end point of a straight line, *short* in comparison with the diameter of the ether envelope. Such a system of two electric poles they call a di-pole, and carbon has four such di-poles. The middle point of each is conceived as bound to the surface of the ether envelope, but freely movable in this; and the di-poles are freely rotatable around their middle points. A farther assumption is that the carbon atom possesses a greater attraction for the positive than for the negative electricity, so that all of the valencies will turn their positive poles toward the carbon atom; and it is also assumed that the positive poles of the valencies have somewhat more strength than the negative. The di-poles of one and the same carbon atom repel each other so that in an isolated carbon



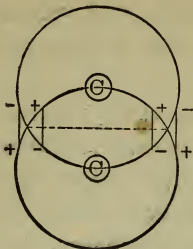
atom there will be equilibrium if the valencies are found in the angles of a regular tetrahedron; but they can be deflected from this position.

When two carbon atoms come so near one another that two di-poles are in immediate juxtaposition, union takes place, and in consequence of the repulsion between like and the attraction between unlike poles, these so arrange themselves that the positive poles of one lie next the negative poles of the other, and vice versa; but since the di-poles are rotatable, two different positions are possible with single linkage, as shown in the following figures:—



In (1) the atoms are freely rotatable around the axis joining the two carbon atoms; but in (2) they are not. By far the more common kind of linkage is that represented in (1),—the kind shown in (2) being only found in cases where the connected radicals are of very nearly the same electrical character, so that there is no strong attraction between them.

Double linkage is represented, according to their theory, by the following figure:—



Auwers has suggested a slight modification of these ideas to account for the fact that the double linkage is not twice as strong as the single. He says that if the ether envelope be considered as only a little larger than the atom itself, the di-poles would then lie nearer the surface of the atom; and in case of double and triple linkage, the di-poles of different atoms could no more lie in immediate juxtaposition, but must act at a certain distance from each other.

These conceptions are somewhat difficult to grasp in full detail, and, until a larger number of well-authenticated cases of isomerism are found to require such an explanation, it seems hardly necessary to adopt any theory to explain limited rotation in singly linked carbon compounds. The general idea, however, of the spherical atom, as charged with four units of electricity, evenly distributed either on its surface or that of its ether envelope, seems to be in good accordance with the facts observed, and recommends itself highly to our judgment. It offers an explanation of the located valence-places, and is in accordance with, or rather a deduction from, Faraday's law. In the present state of knowledge regarding the nature of electricity, any speculations of this kind must be very crude and vague; but the indications of a close relationship between chemical attraction and electricity are strong enough certainly

to make it seem possible that valence may properly be explained in some such way as that pointed out by Meyer and Riecke.

Helmholtz, some time since, to account for the difference in *intensity* of attractive power in different elements, suggested that their electric charges might be held to the atoms with varying degrees of attractive force. Is it not possible, then, that in the same atom, considering its electric charge as made up of definite, located units, some may be held to the atom with less force than others, and thus some of these units be always active, while others are sometimes active and sometimes dormant, thus accounting for varying valence?

None of the theories thus far mentioned take into account the subject of varying valence; and perhaps this is not necessary in the case of carbon, since carbon monoxide is the only compound which is absolutely inexplicable, assuming the valence of carbon to be four, though Nef<sup>1</sup> makes a strong argument in favor of the valence of carbon as two in the iso-cyanides. It has been suggested that the existence of carbon monoxide may be explained equally well by the assumption of the tetravalence of oxygen as by the bivalence of carbon; and Friedel,<sup>2</sup> in support of the former view, gives arguments for the tetravalence of oxygen in  $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$ , and also suggests that it may be to the two extra bonds of oxygen that the existence of substances containing water of crystallization may be due. Even granting, however, the invariability of the valence of carbon, any explanation of this property is of little value unless it can be applied also to other atoms, and therefore should not be of such a nature as to preclude the possibility of varying valence.

<sup>1</sup> Lieb. Ann. d. Chem. 270, 267.

<sup>2</sup> Bull. Soc. Chim. 24, 160, 241.

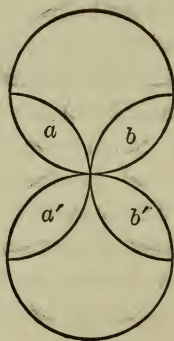
The principal deductions and speculations which have resulted either directly or indirectly from the study of stereo-chemistry have been briefly reviewed in the foregoing. These results may be summed up as follows:—

An atom must be considered either as a material point or a body of finite expansion in space. The teachings of stereo-chemistry are against the former, and in favor of the latter hypothesis. Facts seem to indicate that the atom has a fixed and definite form; this form must be either that of a sphere or a symmetrical polyhedron, and though stereo-chemistry offers no definite teaching on this point, the spherical form seems simpler and, for reasons before given, more probable.

If stereo-chemistry teaches anything in regard to the carbon atom, it is that its attractive force is concentrated in four places, symmetrically arranged with reference to each other and to the centre of the atom. Some investigators regard the valence as a force which can be exerted only in certain definite directions, and symbolize this idea by representing the carbon atom as a bullet, from which four rods proceed in the directions of the angles of a tetrahedron; others think of valence as caused by the existence of four symmetrically arranged portions, which are qualitatively different from the rest of the atom, and which are called valence-places. The nature of valence, considered as a force, is by some supposed to be a particular form of universal gravitation, and by others to be of an electrical or magnetic character.

Some chemists urge that the valence of carbon cannot be *à priori* divided into four portions in the atom, but must be a unified whole until the approach of other atoms separates it into portions. This conception is certainly the one which is most in harmony with our preconceived ideas of atoms and attractive forces; but the teachings of stereo-chemistry do not

justify this conclusion. If we considered only compounds containing a single carbon atom, we should have little difficulty in reconciling the facts with the theory either of inherent or of induced valence-places; but the trouble comes with the consideration of the so-called doubly linked compounds, in which we must account for the impossibility of rotation in opposite directions of the two carbon atoms, and for the fact that the "bonds" cannot be considered as units in the sense of a double bond being twice as strong as a single one. Of these, the former seems the more serious difficulty. In the molecule  $C_2H_4$ , it is conceivable that a certain condition may be induced in the portions of the carbon atom lying next the hydrogen, which should differentiate them from the rest of the atom; but a similar condition would naturally be induced in the adjacent portions of the two carbon atoms, and we find nothing in this to prevent rotation. We can only conceive of the rotation as hindered in case the carbon atoms are held together at two points,  $a a'$  and  $b b'$ , so that the rotation of one atom alone would break this connection.



The reason for the double linkage not being twice as strong as the single is also shown in such a conception as this, for in



the above illustration the valence-places do not come as closely in contact with each other as in single linkage.

Granting, then, the existence of inherent valence-places, there is still diversity of opinion as to whether these are caused by a qualitative difference of matter at these points, or whether they are the results of a polar condition either in the atom itself or its ether envelope; and in regard to this point stereo-chemistry has nothing to say. Having thrown down the postulate of the existence of valence-places, stereo-chemistry withdraws, having apparently no facts to offer in explanation of the cause and nature of such places. These subjects seem at present to be left largely to the domain of pure speculation, though there is an undoubted and proved connection between electricity and valence which cannot be overlooked in any explanation of the latter.

It is plain, then, that stereo-chemistry offers no distinct and definite representation of an atom. It only emphasizes certain attributes of the atom, and has already been very fruitful in stimulating speculations concerning atomic structure and valence. Whether any one of the theories now before the public, or one yet to be evolved, will ever receive experimental verification enough to be yielded universal acceptance, and thus give a definite conception of the atom or not, time alone can tell; but the difficulty of the problem rests in its simplicity, and perhaps none of the solutions yet offered are simple enough to be the true one.



LIST OF BOOKS CONSULTED.<sup>1</sup>

THE following is a list of the principal books and articles on the general subject of stereo-chemistry which have been freely consulted in the preparation of this volume: —

Auwers. Die Entwicklung der Stereo-chemie.

Le Bel. Bulletin de la Société Chimique [2], 22, 337.

Eiloart. Guide to Stereo-chemistry.

Hantzsch. Grundriss der Stereo-chemie.

Van't Hoff. Die Lagerung der Atome im Raume. Herrmann.

Van't Hoff. Dix Années dans l'histoire d'une Théorie.

Van't Hoff's Chemistry in Space. Translated and edited by J. E. Marsh.

Van't Hoff. Bulletin de la Société Chimique [2], 23, 295.

Meyer, R. Jahrbuch der Chemie. 1891 and 1892.

Meyer, V. Ergebnisse und Ziele der stereo-chemischen Forschung. Berichte der deutschen chemischen Gesellschaft, 23, 567.

Pasteur. Ueber die Asymmetrie bei natürlich vorkommenden organischen Verbindungen. Uebersetzt von Ladenburg.

Warder. Proceedings of the American Association for the Advancement of Science, vol. 39, p. 111.

Wislicenus. Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen.

<sup>1</sup> Bischoff's Handbuch der Stereo-chemie has been completed since the above list was made out.

PERIODICALS TO WHICH REFERENCE  
HAS BEEN MADE.

Am. Chem. J. = American Chemical Journal.

Annales de Chim. et de Phys.

Ber. = Berichte der deutschen chemischen Gesellschaft.

Bull. Soc. Chim. = Bulletin de la Société Chimique de Paris.

Compt. rend. = Comptes rendus.

J. Chem. Soc. = Journal of the Chemical Society.

J. pr. Chem. = Journal für praktische Chemie.

Lieb. Ann. d. Chem. = Liebig's Annalen der Chemie.

Monatshefte für Chemie.

Zeit. ph. Chem. = Zeitschrift für physikalische Chemie.

Zeitschrift für Krystallographie.





OCT 02 1967

[illegible]

QD481.R64

SCIII



3 5002 00134 5516

Roberts, Charlotte F.  
The development and present aspects of s

CHEMISTRY LIBRARY

200554

QD  
481  
R64

DOES NOT CIRCULATE



